Water quality and organic matter linkages in waters draining arable fields

Adam Eriksson

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Adam Eriksson

Supervisor: Magdalena Bieroza, SLU, Department of Soil and Environment
Examiner: Jennie Barron, SLU, Department of Soil and Environment

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Swedish University of Agricultural Sciences
Faculty Natural Resources and Agricultural Sciences (NJ)
Department Soil and Environment

Abstract

This study investigated leaching of natural organic matter (NOM) in twelve Swedish arable fields with regards to the quality of dissolved organic matter (DOM) and particulate organic matter (POM), using Absorbance (UV-Vis) and fluorescence spectrometry (EEM). DOM is defined as organic matter (OM) <0.45 µm and POM is defined as OM >0.45 µm. Field sampling was done every two weeks or when flow was available from 2016 until early 2018. Samples were analysed unfiltered and filtered with a 0.45 µm membrane, filtered samples represent DOM properties, whereas by comparing unfiltered and filtered sample results, information about properties of POM was inferred. Nutrients and abiotic parameters were available during the study period, of which nitrogen (N), phosphorus (P), suspended solids (SS), total organic carbon (TOC), dissolved organic carbon (DOC), pH, alkalinity (Alk) and conductivity (Cond) were analysed.

Soil texture and climate were found to be the driving factors behind leaching of NOM. To begin with, clay soils had significantly different leaching patterns than loam soils as they had a higher tendency to leach more autochthonous microbial organic matter while loam soils had a higher input of allochthonous humic matter. Some clay soils were determined to have high losses of adsorbed microbial matter to the surfaces of mineral particles as POM. Some loam soils had highly humifide POM in comparison to the DOM, which could be linked to aggregate formation of humic matter with Ca^{+2} ions. Regarding climate, loam soils in wetter climate had significantly (p<0.05) higher input of humifide terrestrial NOM, while dry climate loam and clay soils had higher input from more microbial sources. Dry periods caused accumulation of labile OM which was rereleased when soils were rewetted.

Seasonal changes in POM and DOM indicated by EEM and UV-Vis absorbance was hard to determine due to high variance in the indices, however the overall seasonal pattern indicated a higher input of autochthonous microbial matter during winter and spring that gradually decreased during summer and autumn until November. An increase in leaching of more labile microbial OM when soils were rewetted during November was observed. The water quality of two clay soils (1D and 11M) were determined to have the lowest water quality among the observation fields. The observation fields had high losses of TOC and high input of labile POM, which was caused by the texture and physical slope of the soil, making the soils vulnerable to leaching and high erosion indicated by the high SS.

Keywords: Natural organic matter (NOM), particular organic matter (POM), dissolved organic matter (*DOM), allochthonous, autochthonous, Florescence index (FIX), Freshness index (BIX), Humification index (HIX), SUVA 254, E2:E3, Spectral Slope, Observation fields, microbial matter, humic matter, unfiltered samples (UF), filtered samples (F45).*

Sammanfattning

Denna här studien undersökte urlakning av naturlig organisk materia (NOM) i tolv svenska åkerfält med avseende på kvaliteten på lös organisk materia (DOM) och partikulärt organiskt material (POM) genom analys av absorbans (UV-Vis) och fluorescerande spektronomi (EEM). DOM definieras som organiskt material (OM) <0,45 µm och POM definieras som OM >0,45 µm. Fältprovtagning gjordes varannan vecka eller när flöde var tillgängligt från 2016 till början av 2018. Prover analyserades ofiltrerade och filtrerade genom ett 0,45 µm-membran; filtrerade prover representerar DOM-egenskaper, medan en jämförelse av ofiltrerade och filtrerade provresultat fastslog egenskaperna för POM. Näringsämnen och abiotiska parametrar var tillgängliga under studieperioden, varav kväve (N), fosfor (P), suspenderade fasta ämnen (SS), totalt organiskt kol (TOC), löst organiskt kol (DOC), pH, alkalinitet (Alk) och konduktivitet (Cond) analyserades.

Markstruktur och klimat visade sig vara drivkrafterna bakom utlakning av NOM. Till att börja med hade lerjord markant olika lakningsmönster än siltjord eftersom de hade en högre tendens att läcka mer autoktont mikrobiellt organiskt material medan siltjord hade ett högre läckage av allokton humifierad materia. Några lerjordar hade höga förluster av mikrobiell materia som adsorberats till mineralpartiklars ytor i form av POM. Vissa siltjordar hade mycket humifierad POM i jämförelse med DOM, vilket kunde kopplas till aggregering av humiskt material med Ca^{+2}-joner. Vad gäller klimatfaktorer hade siltjord i våtare klimat signifikant ($p < 0,05$) högre tillförsel av humiskt material, medan silt- och lerjordar i torrt klimat hade högre tillförsel av mikrobiella källor. Torra perioder orsakade ansamling av labilt OM som lakades ut igen när marken återfuktades.

Säsongsförändringar i POM och DOM indikerade av EEM och UV-Vis-absorbans var svåra att bestämma på grund av höga variationer i index, men det övergripande säsongsmönstret indikerade en högre tillförsel av autokton mikrobiell materia under vinter och vår som gradvis minskade under sommaren och hösten fram till november. En ökning av läckage av mer labil mikrobiell OM när mark återfuktats på nytt i november kunde förmodas. Vattenkvaliteten i två lerjordar (1D och 11M) bestämdes ha den lägsta vattenkvaliteten bland observationsfälten. Observationsfälten hade höga förluster av TOC och hög tillförsel av labil POM, vilket orsakades av markens struktur och den fysiska lutning som gjorde jordarna utsatta för läckage och hög erosion, vilket indikeras av hög SS.

Nyckelord: naturligt organiskt material (NOM), partikulär organiskt material (POM), löst organist material (DOM), allokton, autoktont, *Florescence index (FIX), Freshness index (BIX), Humification index (HIX), SUVA 254, E2:E3, Spectral Slope, Observationsfält, mikrobiellt material,* humiskt *material, unfiltered prover (UF), filterd prover (F45)*

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Abbreviations

A_{254}	Absorbance at 254 nm
BIX	Freshness index
C:T	Fluorescence ratio between peak T tryptophan and peak C humic
CDOM	Chromophoric dissolved organic matter
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
E2:E3	Absorption ratio at 250 nm and 365 nm ratio, indicator of molecular weight and size
EEM	Excitation Emission Matrix
F45	Samples filter through a 0.45 μm membrane
FDOM	Fluorescent dissolved organic matter
FIX	Fluorescence index
HIX	Humification index
MW	Molecular weight
NOM	Natural organic matter
OM	Organic matter
POM	Particulate organic matter
S_{254}	Spectral ultra violet absorption SUVA254
Slope	Spectral slope
SOM	Soil organic matter
TOC	Total organic carbon
UF	Unfiltered samples
UV/Vis	Ultraviolet-visible, refers to absorbance spectroscopy

1. Introduction

The aim of this study is to investigate the quality of natural organic matter (NOM) leaching from twelve Swedish agricultural fields. The relation between particulate organic matter (POM), dissolved organic matter (DOM) and nutrients will be investigated as well as the mechanisms behind leaching of soil organic matter (SOM) and nutrients depending on agricultural practices, climate and soil texture.

1.1. Eutrophication, nutrients and organic matter

Eutrophication is one of the major environmental challenges of the twenty-first century and is a problem for local catchments. Local eutrophication can lead to algae blooms that produce toxins and threaten drinking water, with eventual nutrient loading on coastal waters which threatens marine life in the sea. The Helsinki Commission (HELCOM) is the intergovernmental organisation and convention tasked to protect marine life in the Baltic Sea. The current plan for the protection of the Baltic Sea is the Baltic Sea Action Plan (BSAP), which tasks all surrounding countries with emission targets for nutrients in order to reduce eutrophication. The Swedish Agency for Marine and Water Management (HAV) has tasked the Swedish Environmental Emissions Data (SMED) to collect data of Swedish nutrient loading to the Baltic Sea (HELCOM) (Hansson *et al.,* 2017). The target nutrient load for the Baltic Sea is represented in one of the 16 Swedish environmental goals (Zero eutrophication) set by the Swedish Environmental Protection Agency (SEPA). This goal was set to 2020 and was not achieved. A new goal was initiated in 2015 with the aim of no eutrophication until 2030 and will most likely not succeed (Miljömål 2020).

The agricultural sector is the largest source of anthropogenic nutrient loading to the Baltic Sea in Sweden, and contributes with 19,470 tons of nitrogen (N) and 710 tons of phosphorus (P) every year. Soils are subject to leaching, which is defined as nutrients and organic matter (OM) being transported through surface runoff or through the soil past the root zone and onto cover ditches (Johnsson *et al.,* 2019). Leaching is dependent on soil type and structure as well as climate and agricultural practices such as choice of crop tillage and cultivation (Johnsson *et al.,* 2019).

1.2. Soil organic matter

SOM plays a significant role in the quality and productivity of agricultural soils and is an important part of soil structure, contributing to aggregate blinding, soil stabilization, retention of organic carbon and reduction of erosion (Six *et al.*, 2004; Singh *et al.*, 2016; Bronick & Lal, 2005). The loss of SOM can negatively impact the soil and contribute to eutrophication of water bodies. Leaching of NOM which is presents in all natural waters, as DOM and POM (Hudson *et al.*, 2007). DOM is individual organic molecules that pass 0.45 μm, while POM is larger organic molecules >0.45 μm in a solution (Bolan *et al.*, 2011). The content of POM ranges from single organic structures to coagulations of smaller organic particles as well as organic-mineral structures (adsorption of NOM to mineral surfaces) (Ho *et al.*, 2019). DOM and POM are regarded as energy sources for microbes and a potential pollutant that can lead to eutrophication and development of bacteria and toxic algae (Lmai, 2001). They are moreover a potential risk to drinking water management. OM is not included in the calculations of SMED:s nutrient loading (Hansson *et al.*, 2017).

The degradation of OM is measured in biochemical oxygen demand (BOD) and is the measurement for the utilization of easily attainable organic energy by microorganisms (Hur & Kong, 2007; Hudson *et al.*, 2008). The available energy of the OM that can be used by microorganisms depends on the origin and chemical structure of the OM, as well as the adsorption of it onto mineral surfaces (Singh *et al.*, 2016; Bronick & Lal, 2005). SOM adsorbed onto mineral surfaces is less available for microorganisms than DOM, which is more available to microorganisms (Kalbitz *et al.*, 2005; Swenson *et al.*, 2015). This dynamic changes when adsorbed OM enters an aquatic systems as POM where it becomes more available for degradation (Postnikova, 2015; Marschner & Kalbitz, 2003). Less aromatic microbial OM is more available for microorganisms than terrestrial and humified OM (Bronick & Lal, 2005). Humic substances are directly linked to larger terrestrial OM. The terrestrial matter is in its essence more recalcitrant than the microbial OM due to its structure and requires a more extensive set of enzymes for degradation (Campo, 2019; Lehmann, 2006). Just like the leaching of nutrients, the leaching of OM differs between different soil textures. Clay soils are more vulnerable to water erosion, losses of P and DOM adsorbed onto soil particles, while loam soils are more vulnerable to losses of N due to faster flow through the soil (Johnsson & Hoffman, 1996 &1998; Singh, 2016).

1.3. Fluorescence and absorption indices

The composition and origin of DOM and POM were investigated using Absorption and fluorescence spectrometry, tracking the excision and emission of fluorophores in NOM and the absorption of UV-visible light (UV-Vis) of chromophoric dissolved organic matter (CDOM). The emission excision matrix (EEM) is a known and proven method to investigate the origin and characteristics of fluorophores of fluorescent dissolved organic matter (FDOM) that have a distinct 'fluorescing fingerprint' depending on the fluorescent organic substance (Mcknight *et al*., 2001; Coble, *et al*., 2014; Ohno, 2002). Excitation of wavelengths λ (*ex*) and specific corresponding emissions peak λ (*em*) of the fluorophores in NOM are used to identify the composition and origin of organic molecules.

Fluorescence spectrometry

Humic substances have a longer red-shifting wavelength for emission that increases with humification. The humification index (HIX) (Eq. 1) is used to estimate humification of organic substances (Ohno, 2002; Hudson *et al.*, 2008). Peak C (*ex*) 320–360 nm (*em*) 400-460 nm indicates humification and peak T at (*ex*) 270–280 nm (*em*) 330–370 nm indicates the amino acid tryptophan-containing OM. The ratio between humic (peak C) and labile (peak T) fluorescing-OM, C:T is used to determine the ratio of labile to recalcitrant OM. The chemical structure and stability of DOM is often dependent on its origin. Terrestrially-derived OM is more recalcitrant and has a longer humification and degradation time span. Terrestrial organic molecules such as lignin have a stabile molecular structure that requires special enzymes in order to break the chemical bonds and make the OM more degradable (Campo, 2019; Lehmann, 2006). The Fluorescence index (FIX) (eq. 3) tracks the source and aromaticity of terrestrial and microbial OM, 1.9 indicates microbial derived OM and 1.45 indicates terrestrial OM (McKnight *et al.*, 2001). The freshness index (BIX) (eq. 2) tracks the origin of the OM and is a proxy for its lability (Coble, *et al*., 2014). Low BIX<1 indicates allochthonous derived OM that originates from outside the water stream, while higher BIX>1 indicates autochthonous derived OM that originates from the inside the water stream.

Absorbance UV–Vis spectrometry

NOM absorbs UV-Vis light at different wavelengths λ depending on the characteristics of the organic molecules. Absorbance at λ=254 nm has been used as a general estimation of bulk dissolved organic carbon (DOC) in natural waters (Brandstetter *et al.*, 1996).

Specific ultra-violet absorbance SUVA 254 (S_{254}) normalized for DOC is a determinant for the aromaticity of DOC. S_{254} is an indication for chemical characteristics of DOC but does not indicate the origin or reactivity of DOC (Weishaar *et al.*, 2003). Spectral Slope (Slope) is described as absorption of CDOM as a single exponential model (Eq. 5) indicating molecular weight (MW) (Tardowski *et al.*, 2004). E2:E3 (E2:E3) (Eq. 6) absorption ratio of CDOM indicates MW for humic substances (Peuravuori & Pihlaja, 1997).

Table 1. Fluorescence and Absorbance indices (**Eq. 1-6**, page 26).

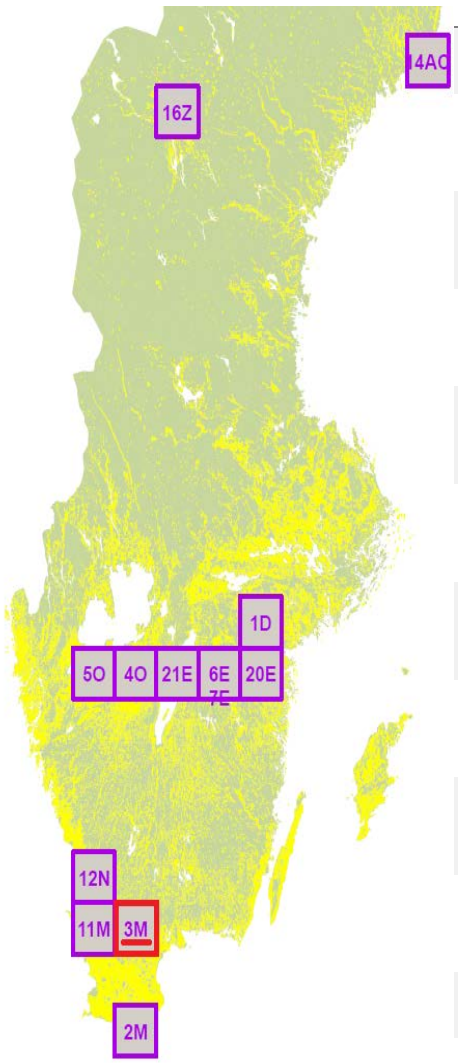
FLUORESCENCE	FULL NAME	SPECIFICS FDOM
FIX	Fluorescence index	Indicator of the origin of NOM, terrestrial and microbial OM
BIX	Freshness index	Amount of freshly produced OM
HIX	Humification index	Humified OM connected to terrestrial OM
C:T	Ration between peak T and peak C	Ratio between tryptophan and humic OM
ABSORBANCE	**Full name**	**Specifics CDOM**
S254	Spectral ultra violet absorption at 254 nm normalized for DOC	Indicator of aromaticity
E2:E3	E2:E3: Absorption ratio at 250 nm and 365 nm ratio	Indicator of molecular weight and size
Slope	Spectral Slope: Expressed as an exponential model	Indicator of molecular weight and size

2. Materials and methods

2.1. Observation fields

Within the program ‘Observation fields on arable lands’ there are thirteen observation fields (Norberg, 2019). This study analyzed the linkage between NOM and nutrients 2016–2018. These observation fields were monitoring nutrient mining, flow and abiotic conditions. The program is part of the national environment monitoring program within the Swedish Environmental Protection Agency (Naturvårdsverket) being responsible for the oversight of the program and the Swedish University of Agricultural Sciences (SLU) being responsible for collecting data (Norberg, 2019). The observation fields also functioned as test sites for different experiments evaluating the impact of agricultural practices on water quality and nutrient losses. Field 3M will not be included in this study due to no available data from the investigated period.

The information about the observation fields is in **Table 1**, including area, soil taxonomy, precipitation and runoff. All fields have a similar setup with water led through surface water intakes to the subsurface drainage and then transported through underdrains from the observation fields to the measuring stations. The measuring stations collected both flow proportional and grab samples that were analysed at SLU Geochemical Lab for total nitrogen (tot-N), nitrite and nitrate (NO_2^- and NO_3^-), total phosphorus (tot-P), SS, TOC, *DOC*, *pH*, alkalinity (Alk) and conductivity (Cond). Flow proportional samples were taken through a Thomson Weir where a Campbell data logger calculated the flow every 30 seconds (Norberg *et al.*, 2015-2018).



FIELD CODE	COUNTY	PRODUCTION AREA
1D	Södermanland	Svealands slättbygder
20E	Östergötland	Götalands norra slättbygder
21E	Östergötland	Götalands norra slättbygder
6E	Östergötland	Götalands norra slättbygder
7E	Östergötland	Götalands norra slättbygder
11M	Skåne	Götalands södra slättbygder
2M	Skåne	Götalands södra slättbygder
12N	Halland	Götalands södra slättbygder
4O	Västergötland	Götalands norra slättbygder
5O	Västergötland	Götalands norra slättbygder
16Z	Jämtland	Nedre Norrland
14AC	Västerbotten	Nedre Norrland

Figure 1. Map of approximate locations of the observation fields. The exact locations of the observation fields cannot be disclosed to protect the farmer's privacy. Observation field 3M in the red square is not included in this study. Green coloured observation field codes are clay soils and orange ones are loam soils. (Figure adopted from Norberg *et al.*, 2017).

Table 2. Observation field area, soil tax, average precipitation and runoff (mm) from the agricultural year 2015/2016-2017/2018. Soil taxonomy is colour coded to respective field code in tables and figures.

FIELD CODE	AREA (HA)	SOIL TAXONOMY	PRECIPITATION (MM)	RUNOFF (MM)
1D	6.6	clay loam	530	160
20E	5.1	clay	475	72
21E	4.4	sandy loam	518	94
6E	10.7	loam	505	125
7E	27.1	silty clay	501	173
11M	22.2	silty clay loam	719	200
2M	33.8	loam	631	245
12N	14.5	sandy loam	684	334
4O	19.3	silty clay loam	575	153
5O	10.9	loam	526	180
16Z	7.4	loam	492	236
14AC	8.4	silt loam	541	268

Observation fields 1D, 11M and 4O were glacial clay soils while 20E and 7E were post glacial soils. Post glacial and glacial soils differ in structure and formation. Glacial soils are fine-grained sediments that were deposited when the inland ice sheet retreated during the last ice age. These soils are often poorer in chalk and organic matter in comparison to the younger post glacial clay, withch were formed by overgrowth of lakes (SGU, 2020).

Information about cropping practices in the observation fields is found in **Table 3.** The study was carried out during the agricultural year 2015/2016-2017/2018. Ley was planted on fields 1D, 11M, 2M and 16Z. Winter wheat was planted on all observation fields except for 1D, 12N, 16Z and 14AC. All observation fields except for 1D and 11M had some sort of tillage practices implemented between cropping seasons. Grain was planted on 12N, 4O, 16Z and 14AC and oats were planted on 1D, 7E and 4O. Winter rape was planted on 21E, 7E and 11M and potatoes were planted on 12N. 21E was the only observation field that was put on fallow. Information on manure/sludge applications is presented in **Table 4.** Observation fields 21E, 6E, 2M, 4O and 5O had no sludge or manure treatment implemented and were left untreated. Cattle manure was spread onto observations fields 1D, 7E, 11M, 16Z and 14AC. Chicken manure was spread on 7E and pig manure was spread on 20E. Sludge was spread on observation field 12N. **Figure 3** shows average daily flow rates from 2016-01-01 until 2018-01-10. Mean precipitation and runoff was lower than average during the spring of 2016 in most parts of Sweden. The majority of runoff occurred during NOV-DEC, with low to no runoff occurring during JUN-OCT (Norberg *et al.*, 2015-2018). The agricultural year of 2017 was wetter than average with most

runoff from the observation fields occurring during JAN-APR and OCT-DEC.

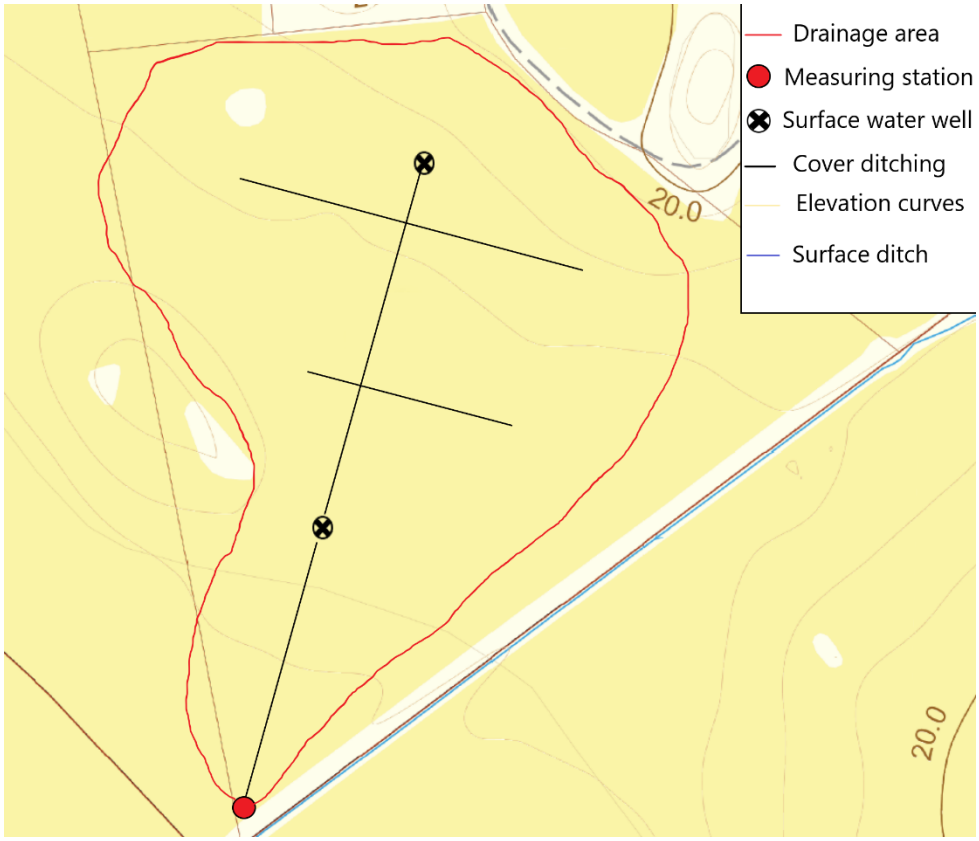


Figure 2. Schematic figure of an observation field. Samples are collected at the measuring station at the end of the cover ditch system. The drainage system diverts for both surface runoff through the surface water wells and soil runoff from the cover ditches.

Table 3. Cropping patterns adopted from *(*Norberg *et al.*, 2015-2018). 2016, 2017 crop harvested during growing season. 2015/2016, 2016/2017 and 2017/2018 agricultural and planted crops during winter season.

FIELD CODE	CROP 2016	CROP 2017	WINTER 2015/2016	WINTER 2016/2017	WINTER 2017/2018
1D	Oats with Ley seeds	Ley	Ley seeds	Ley seeds	Ley
20E	Winter wheat	Winter wheat	Winter wheat	Winter wheat	Tillage
21E	Fallow	Winter rape	Fallow/Tillage	Winter wheat	Winter wheat
6E	Winter wheat	Winter wheat	Winter wheat	Winter wheat	Winter wheat/Tillage
7E	Winter rape/Oats with Ley seeds	Winter wheat/Oats with Ley seeds	Winter rape/Tillage	Ley/Winter wheat	Winter wheat/Ley
11M	Hay/Winter wheat	Ley/ Winter wheat	Winter rape/ Ley seeds	Ley/ Winter wheat	Ley/ Winter wheat
2M	Ley seeds	Winter wheat	Ley seeds	Winter wheat	Cultivated
12N	Potato	Grain	Tillage	Cultivated	-
4O	Oats/ Winter wheat	Winter wheat/ Grain	Tillage/Winter wheat	Winter wheat/Tillage	Tillage/Winter wheat
5O	Winter wheat	Wheat	Winter wheat	Tillage	Winter wheat
16Z	Ley	Ley	Ley	Ley	Tillage
14AC	Grains/Ley	Grain/Ley	Tillage	Tillage/Ley	Tillage/Ley

Table 4. Three first columns are manure and sludge application adopted from (Norberg *et al*, 2015-2018). The last column application of mineral fertilizers in Kg/Ha during 2016-2018.

FIELD CODE	2015/2016	2016/2017	2017/2018	MINERAL FERTILIZER (Kg/Ha)
1D	Liquid cattle manure/spring		Liquid cattle manure /summer	
20E			Liquid pig manure/spring	236
21E				120
6E				204
7E	Liquid cattle manure /spring and winter and dry cattle manure /autumn	Liquid cattle manure /spring winter and cattle manure /autumn	Liquid chicken and cattle manure /spring	28
11M	Liquid cattle manure /spring and autumn	Liquid cattle manure /summer and autumn	Liquid cattle manure/summer and autumn	236
2M				32
12N	Sludge (biogas)/spring	Sludge (biogas)/spring	Sludge (biogas)/spring	84
4O				130
5O				126
16Z	Liquid Cattle manure /autumn	Liquid Cattle manure /autumn		80
14AC	Liquid Cattle manure /spring			303

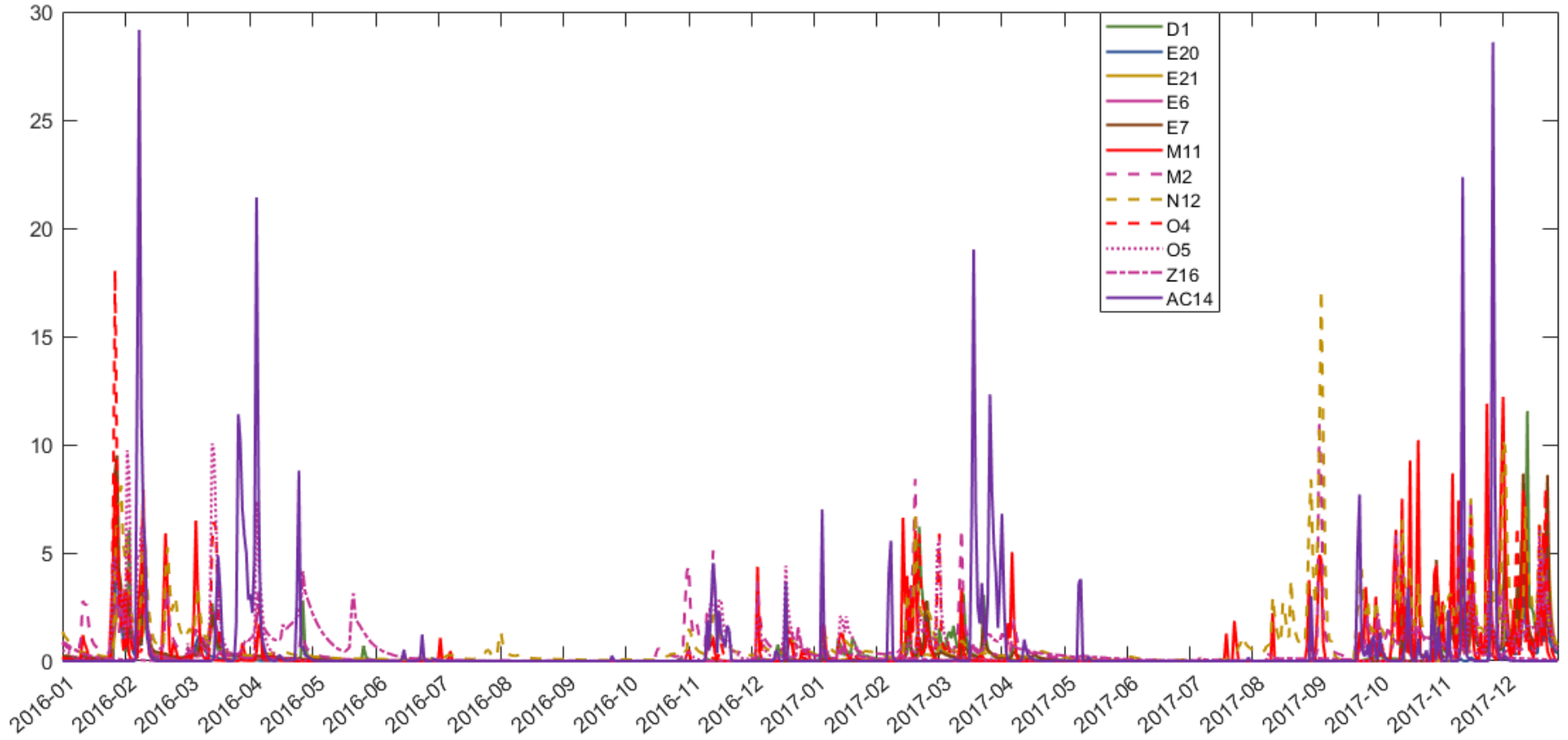


Figure 3. Average daily flow rates from 2016-01-01 until 2018-01-10 Y AXIS. Peak flow rates are observed during winter and spring 2016, 2017 and autumn 2017. Flow data obtained from jordbruksvatten.slu.se (30.08.2020).

2.2. Statistical analyses

Water samples collected from the runoff water of the observation fields were transported to the lab at Ultuna (the headquarters and main campus of SLU), stored in a dark cooler at 8°C and analysed within 8 weeks of collection. Thereafter, samples were separated into unfiltered (*UF*) and filtered (*F45*); filtration was done through a 0.45 μm membrane. The samples were analysed using fluorescence and absorbance spectroscopy and a number of parameters were calculated: fluorescence indices and absorbance indices. Nutrient, abiotic parameters and water quality data ; Alk, Cond, pH, tot N, tot P, NO_2^-/NO_3^-, Suspended solids (SS), TOC and flow were taken from the long term data base *Fields of observation on arable land* available at (jordbruksvatten.slu.se). Data on the soil organic carbon in the observation fields was not available in this study.

Samples from the drainage ditches were collected when the flow from the observation fields was active, with two weeks intervals starting from the second week of 2016 and ending in the first week of 2018. Samples were also collected during low flows. The reason that there are more *UF* samples than *F45* samples is that too little water was collected in the sample bottles. **Table 5.** shows the total number of samples for all observation fields in relation to months. Fewer samples were taken during summer due to no active flow coming from the observation fields' drains.

Table 5. Seasonal distribution of sampling. Total number of filtered (*F45*) and unfiltered (*UF*) samples per month.

	JAN	FEB	MAR	APR	MAJ	JUN	JUL	AUG	SPE	OCT	NOV	DEC
F45	33	41	44	44	47	47	24	22	23	35	24	17
UF	35	42	45	45	42	47	30	22	22	37	36	40

Fluorescence was measured using Aqualog (Horriba, US) spectrophotometer, measuring excitation wavelengths between 240-600 nm and emission wavelengths between 211-620 nm. Absorbance was measured using the AVasoft (Avaspec-3648) spectrophotometer, with absorbance wavelengths between 180-800 nm. A Raman blank (distilled water) in a 10x10 mm cuvette was used as reference to calibrate the machines before every machine run.

Table 6. Number of samples *UF* and *F45* and what year they were collected.

	TOTAL SAMPLES		2016		2017		2018
FIL	*UF*	*F45*	*UF*	*F45*	*UF*	*F45*	*UF*
1D	29	25	10	10	19	15	
20E	30	25	12	12	17	13	1
21E	15	15	14	15			1
6E	54	49	26	26	27	23	1
7E	20	17	9	10	10	7	1
11M	43	37	21	20	21	17	1
2M	52	51	26	28	25	23	1
12N	51	46	26	24	24	22	1
4O	34	33	16	17	17	16	1
5O	52	45	28	26	23	19	1
16Z	45	41	21	19	23	22	1
14AC	18	17	7	7	11	10	
1D	443	401	216	214	217	187	10

The data were analysed using MATLAB (R2019b) and Microsoft Excel 2010. Data were first tested for normality using the one-sample Kolmogorov-Smirnov test with a 95% significance level. Due to the distorted data that did not follow normal distribution, the ANOVA one way analysis could not be used; instead the Kruskal-Wallis one-way analysis was used to differentiate significant differences in spatial variation between observation fields and seasonal differences between the sampling months. Spearman's rank correlation (ρ) was used since the premises for using Persons correlation were heavily violated.

EEM was calibrated by removing the Raman scatter and implementing inner-filter corrections. The calibration was done automatically by the Aqualog (Horriba, US) spectrometer. Data for different peak intensity areas with corresponding excitation and emission wavelengths together with absorbance were collected as a part of monitoring the quality of DOM in the waters of the observation fields. This study will be focusing on the following EEM indices and absorption indices.

EEM indices:

- Ratio between peak C humic-like and peak T tryptophan-like forming the C:T ratio.

- Florescence index (FIX) (Eq.3), (Mcknight *et al*., 2001).
- Freshness index (BIX) (Eq.2), (Coble, *et al*., 2014).
- Humification index (HIX) (Eq.1), (Ohno, 2002).

Absorbance indices:

- Specific ultraviolet absorbance (S_{254}) (Eq.4), (Weishaar *et al.*, 2003).
- E2:E3 ratio (Eq.6), (Puhani & Pihlaja, 1996)
- Spectral slope (Slope) (Eq.5), (Twardowski, *et al.*, 2004).
- Absorption 254 (A_{254}) correlated to bulk DOC and was included in the study and read directly from the AVasoft-spectrophometer (Brandstetter, A., 1996).

$$HIX_{ex255} = \frac{(\sum I\ em\ 435{-}480)}{(\sum(I\ em\ 300{-}345)+(\sum(I\ em\ 435{-}480)\ )} \quad \text{Eq.1}$$

$$BIX_{ex310} = \frac{(\sum I\ em\ 380)}{(\max I\ (em\ 420{-}435)} \quad \text{Eq.2}$$

$$FIX_{ex370} = \frac{(I\ em\ 450)}{(I\ em\ 500)} \quad \text{Eq.3}$$

The specific ultraviolet absorbance S_{254} was calculated according to Weishaar *et al.* 2003 at λ=$_{254}$ (A_{254}) (Eq.4). The DOC was used for *F45* and TOC was used for *UF* samples.

$$S_{254} = \frac{A_{254}}{TOC/DOC} * 100 \quad \text{Eq.4}$$

There are different functions to calculate Spectral Slope (Slope) (Twardowski *et al.*, 2004). In this study the spectral Slope is expressed as a single exponential function (Eq.5) according to (Twardowski *et al.*, 2004). The spectral Slope was calculated between wavelengths that are applicable to many different types of water (S_{275}-S_{295} nm and S_{350}-S_{400} nm). a_λ Is the absorbance coefficient at wavelength λ, $a_{\lambda \mathrm{r}}$ is the adsorption coefficient at the reference wavelength and S is the spectral Slope (nm^{-1}).

$$a_\lambda = a_{\lambda \mathrm{r}} e^{-S(\lambda-\lambda_r)} \quad \text{Eq.5}$$

The ratio E2:E3 (Eq.6) was calculated according to (Peuravuori & Pihlaja, 1997). An increase in E2:E3 corresponds to a decrease in the molecular size and aromaticity for the humic fraction in aquatic systems.

$$E2{:}E3 = \frac{\mathrm{A250\ nm}}{\mathrm{A365\ nm}} \quad \text{Eq.6}$$

3. Results

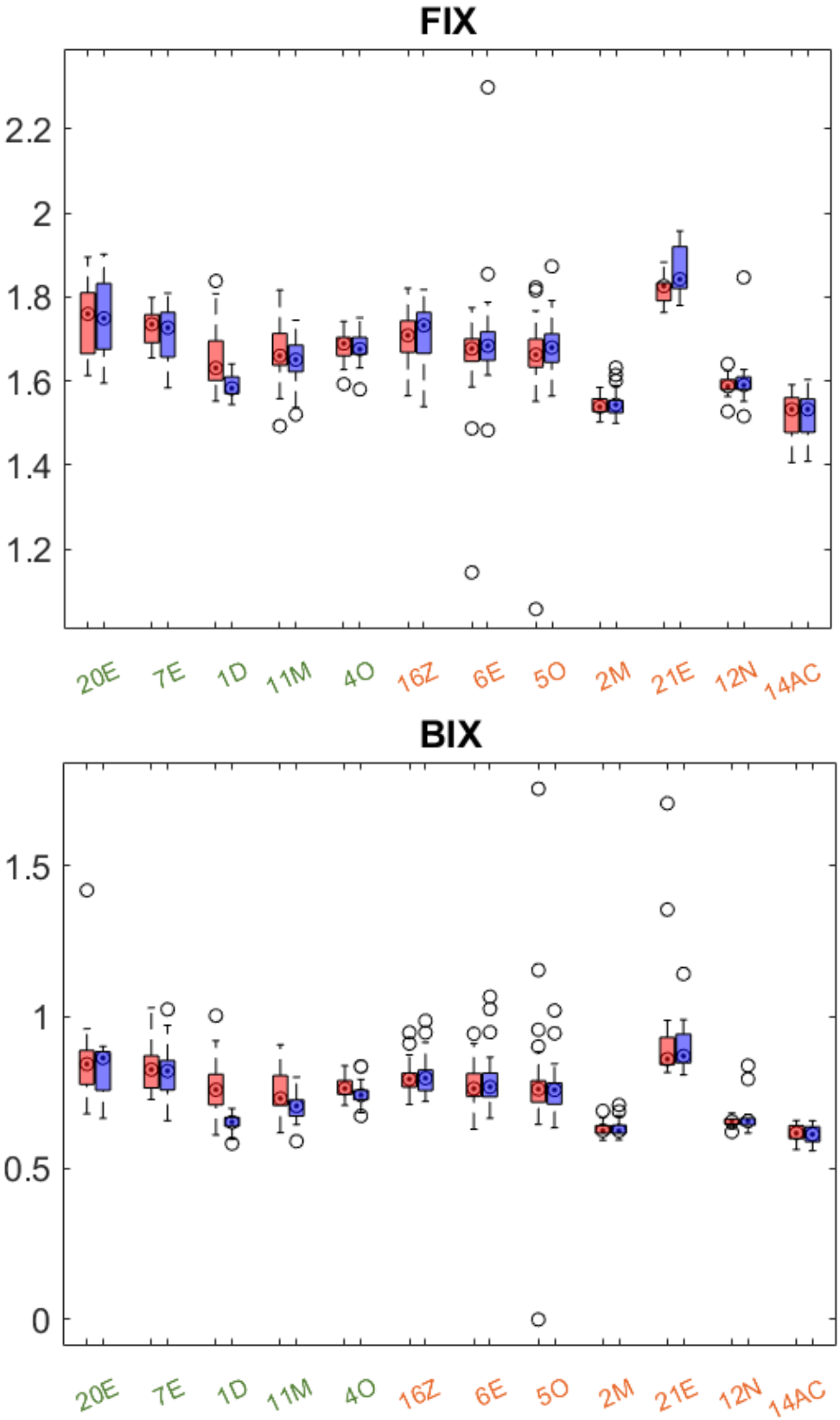
3.1. Spatial distribution

The Kruskal-Wallis one-way analysis of variance between observation fields, months and indices with significance at $p<0.05$ is shown in **Appendices 1-3.** Specific values for each observation field regarding the fluorescence, absorbance indices and nutrition/abiotic parameters can be found in **Tables 7 & 8** respectively. **Figures 4-5** show the observation fields in order of soil taxonomy going from the most fine textured soil 20E to the most course textured soil 14AC; green text=clay soil, orange text=loam soil. Observation fields unmarked by $_{UF}$ or $_{F45}$ indicate significant differences for both fractions.

Spatial distribution of fluorescence indices

Most observation fields had a similar input from both microbial and terrestrial DOM sources, with average BIX 0.74 and FIX 1.67 across all observation fields. Both indices showed similar results for all observation fields, with high values indicating OM produced from autochthonous microbial sources (Mcknight *et al*., 2001; Coble, *et al*., 2014). There were however some differences between observation fields 2M, 12N, 14AC and $1D_{F45}$ that had significantly lower ($p<0.05$) input from autochthonous microbial sources than other observation fields. 21E had higher input from freshly produced microbial material with significantly higher ($p<0.05$) FIX and BIX values than all other observation fields (except for 20E, 7E and 16Z) **Figure 4**. The HIX index had reversed results to FIX and BIX **Figure 4**, with an average value of 0.9 indicating a high humification rate across most observation fields. Samples $2M_{UF}$ and $12N_{UF}$ had significantly higher ($p<0.05$) HIX compared to other observation fields. The *UF* samples indicated a lot more input of OM with a lesser rate of humification. $1D_{UF}$ was significantly different ($p<0.05$) compared to other observation fields except for $11M_{UF}$ and $4O_{UF}$. Large differences were observed between fields and samples for the ratio of peak C to peak T fluorescence (C:T) in **Figure 4**. The C:T indicates ratio of humic-like fluorescence to microbially-derived fluorescence and lower values indicate recently produced OM. Fields 2M and 12N had higher C:T ratios, whereas fields 1D and 11M had lower but

variable C:T values for *UF* samples. Most of the fields showed C:T ratios of 1.8, which was similar for both *UF* and *F45*.



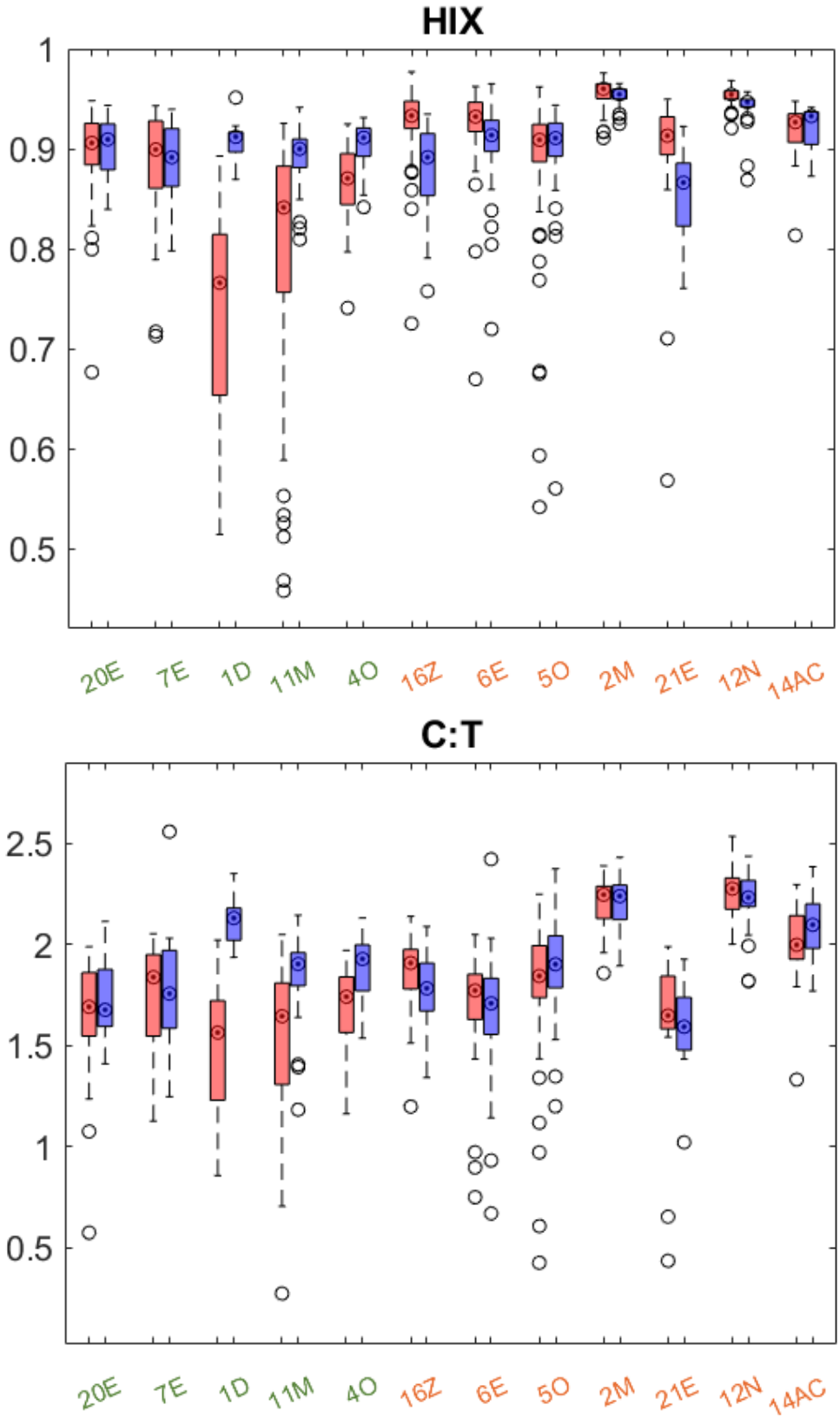


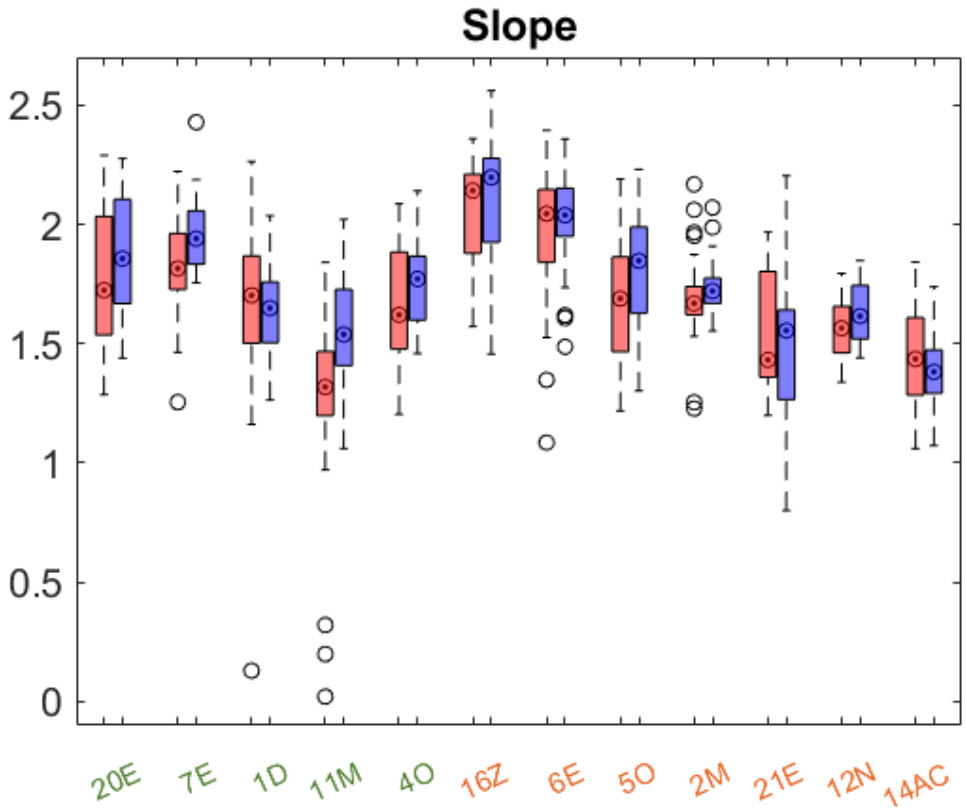
Figure 4. Display box-plots for BIX, FIX, HIX and C:T. The edges of the box denote the 25th and 75th percentile respectively. Red box left *UF*, blue box right *F45*. All indices are unitless (**Eq. 1-3).**

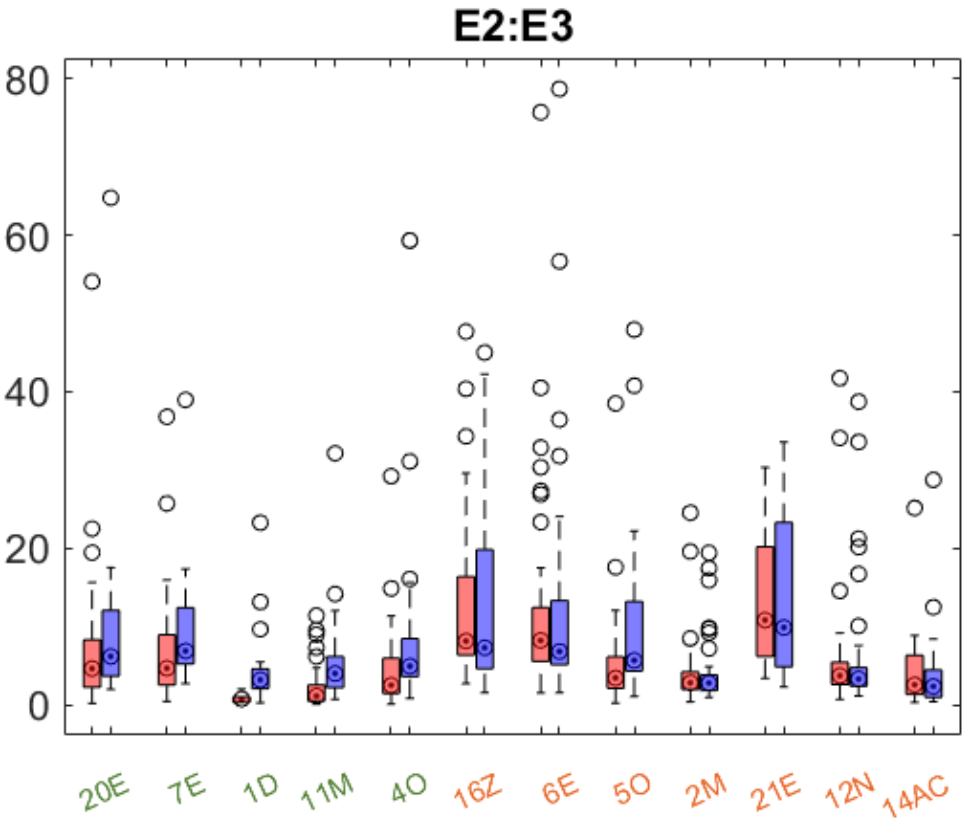
Spatial distribution of absorbance indices

Several differences between individual observation fields were observed for the Slope and E2:E3 ratio (**Figure 5**), with higher values indicating low MW for OM. Observation fields 16Z and 6E had significantly higher values for spectral Slope compared to other observation fields, except for 20E and 7E. *1D$_{UF}$* and *11M $_{UF}$* had significantly lower values for E2:E3 compared to other observation fields. The S_{254} shows the aromaticity for OM in aquatic systems. Observation field 1D$_{UF}$ and 14AC$_{UF}$ had significantly (p<0.05) higher values compared to other observation fields. Observation fields 7E $_{UF}$ and 16Z $_{UF}$ had significantly higher S_{254} compared to 1D$_{UF}$, 2M $_{UF}$, 5O$_{UF}$ and 14AC$_{UF}$. A_{254} tracking the bulk TOC had similar results to that of S_{254}, where higher values of A_{254} indicate a higher concentration of TOC. 1D$_{UF}$ had significantly (p<0.05) higher values to that of other observation fields except for 11M $_{UF}$ and 14AC $_{UF}$. Observation field 21E$_{UF}$ and 16Z$_{UF}$ had significantly lower A_{254} except for 20E$_{UF}$, 6E$_{UF}$ and 7E$_{UF}$.

Effect of sample filtration

There were few significant differences between the *UF* and *F45* samples collected from the same observation fields. The *F45* samples had significantly (p<0.05) lower TOC concentrations. 1D stood out in regards to the absorbance and the effects of filtering, and had significantly different results depending on filtering for most indices: FIX, HIX C:T, E2:E3, S_{254} and A_{254}. The results for 1D show that there was a significantly (p<0.05) higher abundance of microbial low humified material with high MW and aromaticity in the *UF* samples, with the *F45* samples indicating OM with humified terrestrial origin. 11M had significantly different results between *UF* and *F45* for C:T, E2:E2 and A_{254} and was nearly significant for HIX. 11M$_{UF}$ had the same pattern as 1D$_{UF}$ high microbial matter, low input from humified material and high MW, with 11M$_{F45}$ indicating terrestrial humified material just as 1D$_{F45}$. 16Z had a significantly different indication for HIX with a higher amount of humic material in the *UF* samples compared to the *F45*.


Slope
2.5
2
1.5
1
0.5
0
20E
7E
1D
11M
4O
16Z
6E
5O
2M
21E
12N
14AC


E2:E3
80
60
40
20
0
20E
7E
1D
11M
4O
16Z
6E
5O
2M
21E
12N
14AC

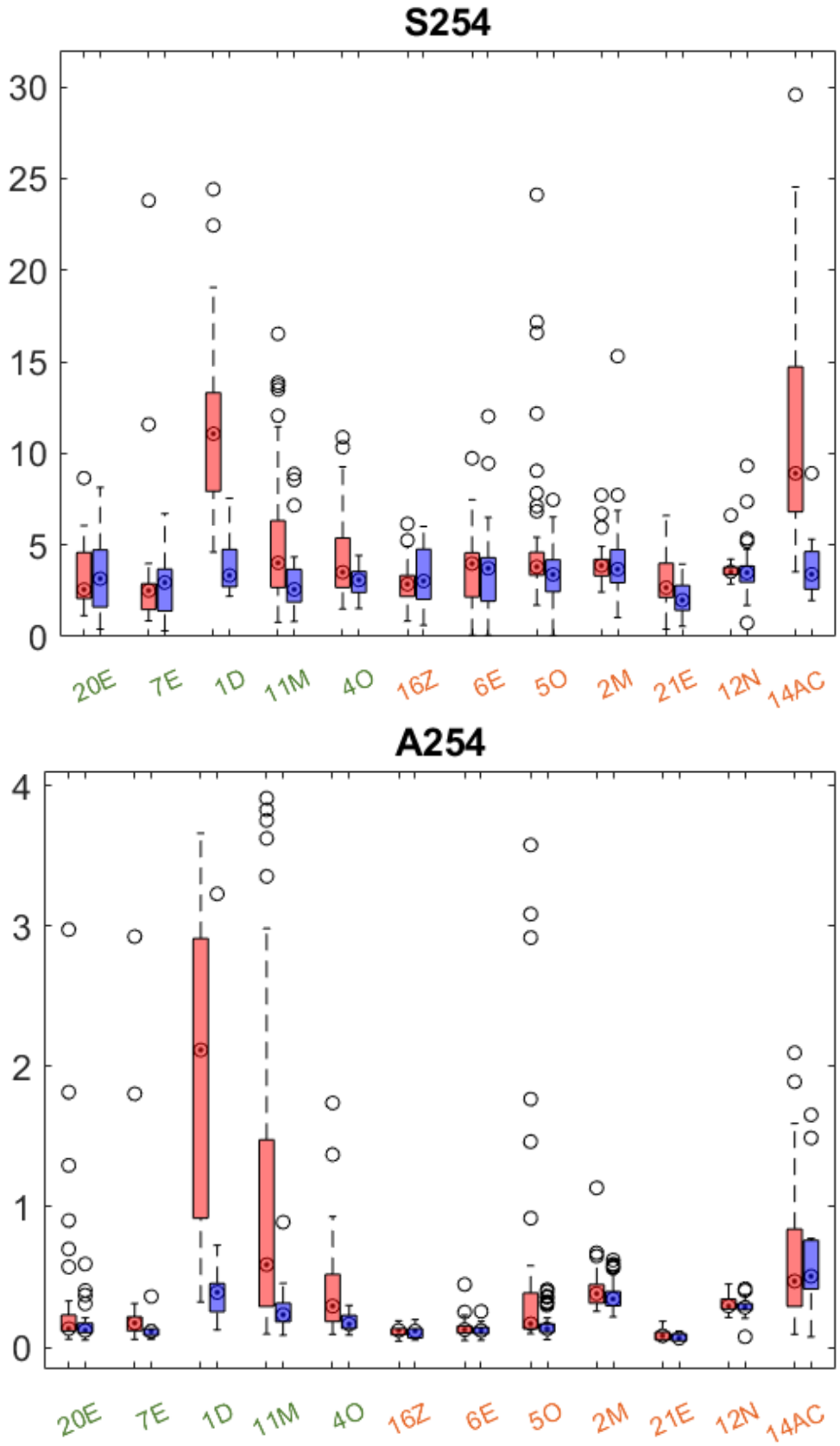


Figure 5. Display box-plots for CDOM Slope, E2:E3, C:T and S_{254} The edges of the box denote the 25th and 75th percentile respectively. Red box left *UF*, blue box right *F45*. All indices are unitless (**Eq. 4-6).**

Table 7. Median value (m) and standard deviation (S) for absorbance and fluorescence indices.

			D1	***20E***	***21E***	***6E***	***7E***	***11M***	***2M***	***12N***	***4O***	***5O***	***16Z***	***14AC***
FIX	*UF*	m	1.63	1.76	1.83	1.68	1.74	1.66	1.54	1.59	1.69	1.66	1.71	1.53
		S	0.08	0.08	0.03	0.09	0.04	0.06	0.02	0.02	0.03	0.10	0.06	0.06
	F45	m	1.58	1.75	1.84	1.68	1.73	1.65	1.54	1.59	1.68	1.68	1.73	1.53
		S	0.03	0.09	0.06	0.10	0.07	0.05	0.03	0.04	0.04	0.05	0.07	0.06
BIX	*UF*	m	0.76	0.84	0.86	0.76	0.83	0.73	0.62	0.65	0.76	0.76	0.79	0.62
		S	0.09	0.13	0.25	0.06	0.08	0.06	0.02	0.01	0.03	0.19	0.05	0.03
	F45	m	0.65	0.86	0.87	0.77	0.82	0.71	0.62	0.66	0.74	0.76	0.80	0.61
		S	0.03	0.08	0.09	0.08	0.09	0.04	0.02	0.04	0.04	0.07	0.06	0.03
HIX	*UF*	m	0.77	0.91	0.91	0.93	0.90	0.84	0.96	0.95	0.87	0.91	0.93	0.93
		S	0.14	0.06	0.10	0.04	0.07	0.16	0.01	0.01	0.04	0.09	0.04	0.03
	F45	m	0.91	0.91	0.87	0.91	0.89	0.90	0.95	0.95	0.91	0.91	0.89	0.93
		S	0.02	0.03	0.04	0.04	0.04	0.03	0.01	0.02	0.02	0.06	0.04	0.02
C:T	*UF*	m	1.56	1.69	1.65	1.77	1.84	1.64	2.25	2.27	1.74	1.84	1.91	2.00
		S	0.33	0.30	0.44	0.26	0.27	0.40	0.12	0.12	0.18	1.32	0.18	0.21
	F45	m	2.13	1.68	1.59	1.71	1.76	1.90	2.24	2.23	1.93	1.90	1.78	2.10
		S	0.11	0.20	0.23	0.28	0.31	0.20	0.13	0.13	0.15	0.23	0.18	0.15
E2:E3	*UF*	m	0.72	4.61	10.80	8.21	4.65	1.11	2.79	3.70	2.47	3.41	8.13	2.54
		S	0.57	10.30	8.86	12.08	9.07	2.67	4.11	7.08	5.64	5.78	10.18	5.78
	F45	m	3.16	6.15	9.86	6.79	6.86	3.98	2.77	3.28	4.92	5.65	7.27	2.33
		S	4.80	12.44	10.77	13.92	8.65	5.47	4.00	7.85	14.03	9.44	10.64	7.00
Slope	*UF*	m	1.70	1.72	1.43	2.04	1.81	1.32	1.67	1.56	1.62	1.69	2.14	1.44
		S	0.41	0.29	0.25	0.25	0.23	0.45	0.15	0.12	0.23	1.46	0.21	0.22
	F45	m	1.65	1.86	1.55	2.04	1.94	1.54	1.72	1.62	1.77	1.85	2.20	1.38
		S	0.19	0.26	0.36	0.22	0.18	0.24	0.10	0.12	0.18	0.24	0.28	0.17
S_{254}	*UF*	m	11.07	2.57	2.67	3.98	2.51	4.02	3.88	3.54	3.51	3.81	2.86	8.91
		S	7.83	1.81	1.69	1.88	5.34	4.09	0.95	0.53	2.47	4.34	1.13	7.51
	F45	m	3.34	3.16	1.99	3.73	2.95	2.73	3.68	3.49	3.09	3.39	3.03	3.40
		S	1.68	16.21	1.01	2.20	1.86	2.10	20.28	1.42	30.16	1.65	1.48	2.25
A_{254}	*UF*	m	2.12	0.13	0.08	0.13	0.17	0.59	0.38	0.29	0.29	0.17	0.12	0.47
		S	1.07	0.63	0.04	0.06	0.71	1.21	0.15	0.05	0.36	0.76	0.04	0.58
	F45	m	0.39	0.12	0.06	0.12	0.11	0.23	0.34	0.28	0.16	0.13	0.12	0.51
		S	0.59	0.13	0.03	0.04	0.07	0.14	0.10	0.06	0.05	0.09	0.04	0.41

Table 8. Median values (m) and standard deviations (s) for samples. TotN, NO_2+ NO_3+, TotP, SS TOC (mg/l); Alk (mmol/l); Cond (mS/m) and Flow (mm). These are not the total averages but the averages from when FDOM and CDOM samples were collected.

		Alk	Cond	pH	TotN	NO_2+NO_3	TotP	SS	TOC	FLOW
1D	m	0.60	14.40	6.67	5.61	3.56	0.45	222.40	15.60	0.21
	s	0.45	5.91	0.38	6.92	7.16	0.34	165.55	10.75	1.40
20E	m	5.74	95.70	7.63	8.98	8.01	0.06	10.50	5.10	0.01
	s	1.92	23.98	0.25	5.71	4.92	0.12	64.24	5.85	0.27
21E	m	5.77	74.35	7.25	15.05	14.20	0.00	1.00	2.65	0.04
	s	0.66	5.08	0.31	5.43	4.77	0.22	120.84	3.50	113.83
6E	m	4.83	77.30	7.95	6.68	6.28	0.01	2.55	3.32	0.00
	s	0.56	5.93	0.22	3.86	3.60	0.02	4.69	24.27	0.29
7E	m	3.55	51.50	7.41	7.80	6.49	0.24	63.20	7.70	0.12
	s	0.45	2.89	0.07	4.42	3.87	0.21	154.75	4.93	0.23
11M	m	2.85	48.80	7.40	8.55	7.21	0.33	185.80	14.35	0.03
	s	1.12	14.15	0.31	14.66	14.50	0.79	389.72	13.64	1.54
2M	m	5.53	64.00	7.70	5.12	4.39	0.04	13.55	9.55	0.32
	s	0.80	6.60	0.31	2.24	2.08	2.24	29.69	2.92	0.88
12N	m	1.01	42.25	6.50	18.40	17.80	0.01	2.85	8.35	0.41
	s	0.19	8.48	0.23	7.11	6.87	0.01	3.96	1.41	1.04
4O	m	0.52	28.30	6.86	12.50	12.00	0.18	94.40	7.60	0.02
	s	0.44	5.53	0.31	6.65	8.01	0.18	72.72	4.30	0.77
5O	m	2.43	37.30	7.20	7.26	6.65	0.06	13.00	5.20	0.01
	s	0.68	5.09	0.33	4.89	4.74	0.29	252.54	6.56	0.82
16Z	m	6.33	69.00	7.24	2.82	2.51	0.01	2.40	4.10	0.13
	s	0.58	5.99	0.18	1.13	1.05	0.04	4.27	1.32	0.53
14AC	m	0.15	45.50	5.01	3.45	2.96	0.03	16.60	5.30	0.13
	s	0.37	6.36	0.52	1.16	1.07	0.02	9.54	2.30	6.81

3.2. Temporal changes in OM

Figure 6 & 8 show the seasonal variation for FIX, BIX, HIX, C:T, E2:E3, Slope, S_{254} and A_{254} by packing results from all years and observation fields into each month. The red (*UF*) and blue (*F45*) trend lines show the median with corresponding boxplots displaying 25^{th} and 75^{th} percentile. All values except for Slope have been logged to showcase the seasonal variation of the indices. Specific differences between months are reported in **Appendix 1.** Observation fields unmarked by $_{UF}$ or $_{F45}$ indicate significant differences for both fractions.

The overall seasonal pattern for the fluorescence indices FIX, BIX and C:T indicates a significantly lower input of freshly produced microbial matter in the month of OCT. FIX_{UF} indicates a significant higher value in JAN, while BIX_{UF} and $C:T_{UF}$ indicate a significantly higher value in MAY. HIX had no significant seasonal variation (**Figure 6**).

The seasonal pattern for E2:E3 was heavily fluctuating with different patterns for *UF* and *F45*. $E2:E3_{UF}$ had significantly high values in the month of JAN/APR and low values in FEB/MAY. $E2:E3_{F45}$ had significantly high values in NOV with low values in FEB, JUL and SEP. $Slope_{F45}$ had no significant seasonal difference between months, while $Slope_{UF}$ indicated significantly lower results in NOV and higher values during JAN, MAY, JUN. AUG and DEC (**Figure 7**).

The seasonal pattern for S_{254} indicates a significantly higher input of OM with lower aromaticity in the beginning of the year in the month of JAN. S_{254F45} also had significantly lower values in FEB.

The A_{254} was at its peak during winter, late spring and summer. MAY and JUN had significantly higher readings for A_{254}. There was a lag time between DEC and JAN during the high readings in the winter period, with the *UF* samples indicating high readings during JAN and *F45* (**Figure 8**).

Nutrients, TOC and flow rates have patterns of increase during autumn, with elevated values during winter and lower during summer, no significant differences were however recorded (**Figure 9**).

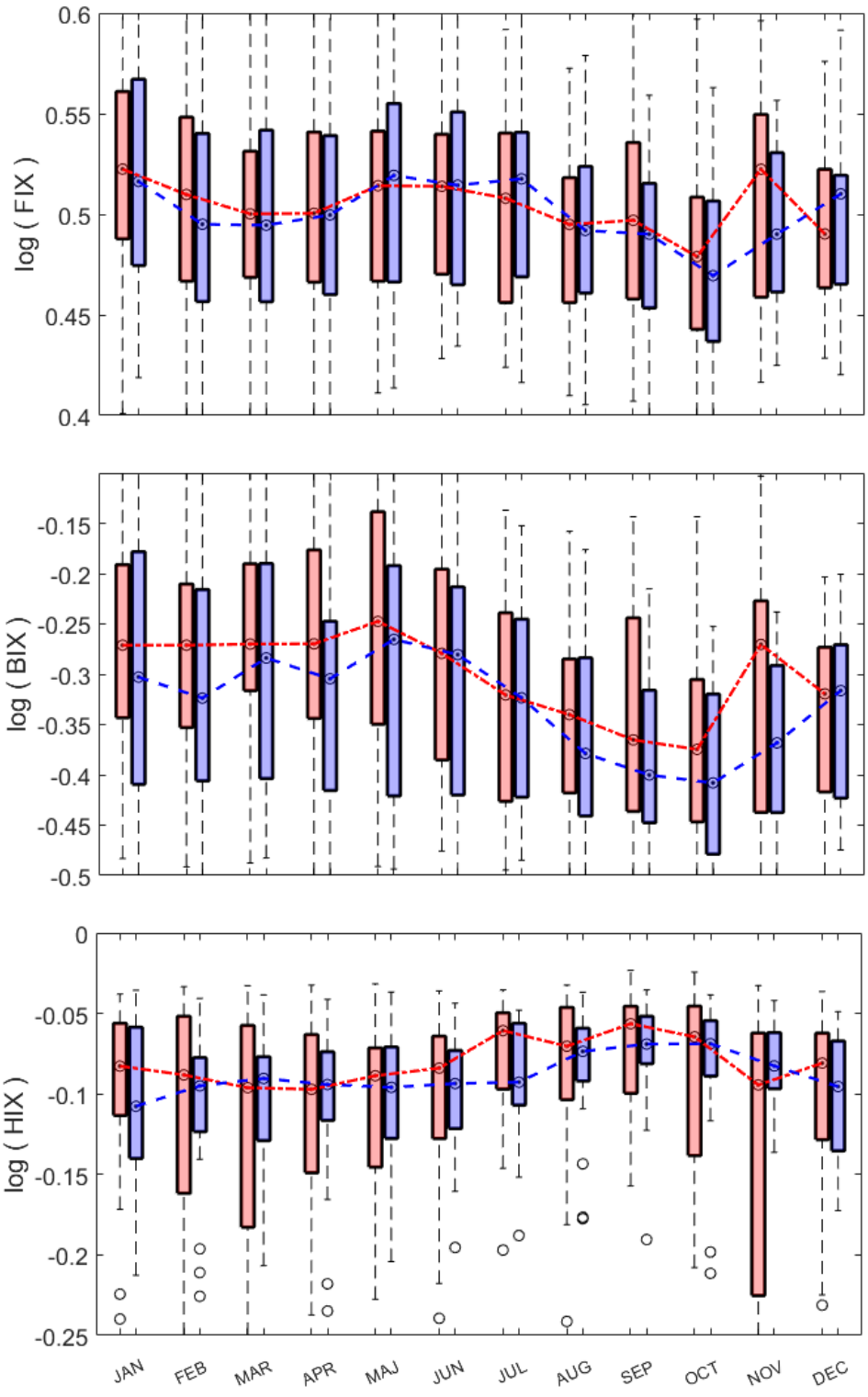


Figure 6. Seasonal variation for FIX, BIX and HIX. Box plot with trendline. Red box left *UF*, blue box right *F45*.

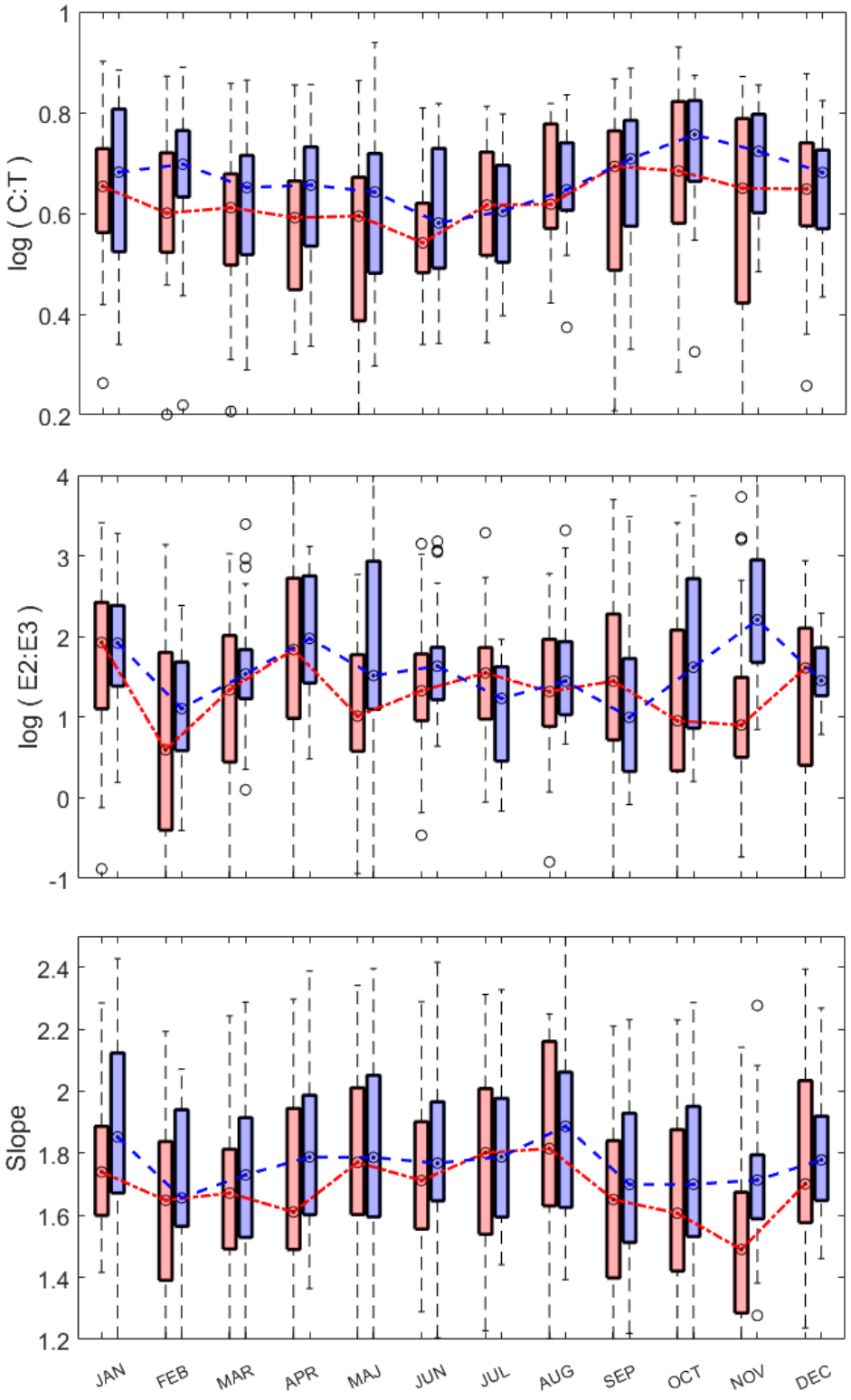


Figure 7. Seasonal variation for C:T, E2:E3 and Slope. Box plot with trendline. Red box left *UF*, blue box right *F45*.

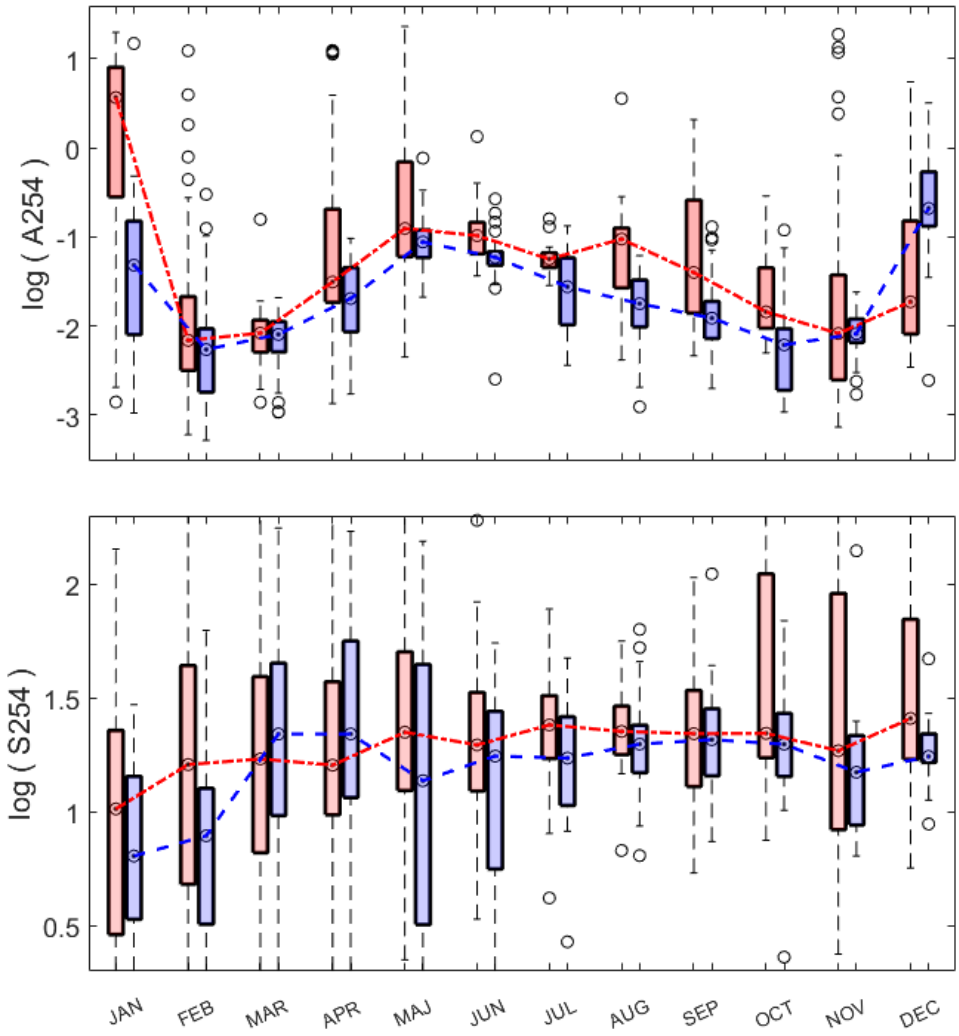


Figure 8. Seasonal variation for A_{254} and S_{254}. Box plot with trendline. Red box left *UF*, blue box right *F45*.

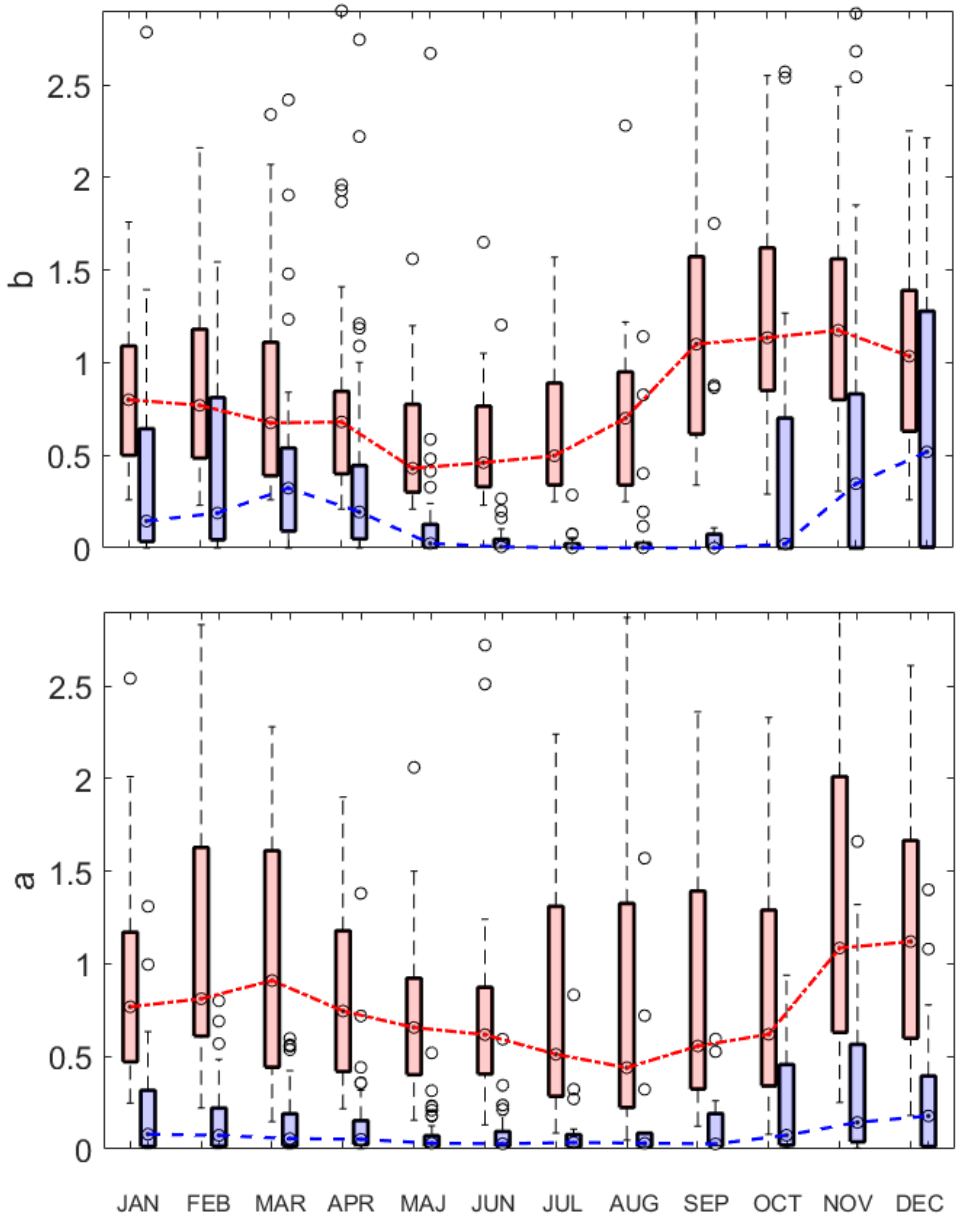


Figure 9. Box plot with trendline. (a). Bottom figure; red tot-N (cg/l) and blue tot-P (mg/l). (b). Upper figure; red TOC (cg/l) and blue flow (mm).

Table 9. Medina (m) and standard deviation (S) FIX, BIX, HIX, C:T, E2:E3, Slope, S_{254} and A_{254} total samples.

			Jan	*Feb*	*Mar*	*Apr*	*Maj*	*Jun*	*Jul*	*Aug*	*Sep*	*Oct*	*Nov*	*Dec*
FIX	*UF*	m	1.68	1.66	1.66	1.63	1.67	1.68	1.65	1.64	1.61	1.61	1.67	1.62
		S	0.1	0.09	0.1	0.1	0.09	0.06	0.08	0.06	0.1	0.16	0.09	0.07
	F45	m	1.68	1.64	1.64	1.65	1.68	1.67	1.68	1.64	1.63	1.60	1.63	1.67
		S	0.14	0.10	0.09	0.10	0.10	0.09	0.09	0.07	0.07	0.08	0.07	0.07
BIX	*UF*	m	0.76	0.76	0.76	0.76	0.77	0.76	0.72	0.68	0.67	0.7	0.75	0.72
		S	0.1	0.08	0.09	0.12	0.21	0.07	0.08	0.06	0.09	0.15	0.09	0.06
	F45	m	0.74	0.72	0.75	0.74	0.77	0.76	0.72	0.68	0.67	0.66	0.69	0.73
		S	0.10	0.09	0.12	0.09	0.11	0.09	0.07	0.07	0.07	0.08	0.06	0.06
HIX	*UF*	m	0.92	0.92	0.92	0.92	0.92	0.93	0.94	0.94	0.94	0.93	0.91	0.92
		S	0.04	0.11	0.08	0.08	0.08	0.04	0.03	0.03	0.12	0.14	0.11	0.06
	F45	m	0.90	0.91	0.91	0.91	0.91	0.91	0.91	0.93	0.93	0.93	0.92	0.91
		S	0.05	0.04	0.04	0.04	0.04	0.03	0.03	0.03	0.03	0.07	0.02	0.03
C:T	*UF*	m	1.97	1.9	1.87	1.84	1.77	1.8	1.81	1.85	2.02	1.99	1.95	1.97
		S	0.34	0.36	0.33	0.37	0.43	0.3	0.25	0.22	0.43	1.8	0.39	0.26
	F45	m	1.98	2.01	1.92	1.93	1.90	1.79	1.83	1.91	2.03	2.13	2.06	1.98
		S	0.36	0.26	0.29	0.26	0.30	0.24	0.21	0.21	0.26	0.31	0.21	0.23
E2:E3	*UF*	m	6.86	2.5	4.84	7.3	2.61	5.61	4.49	3.89	3.64	2.48	2.22	5.01
		S	9.86	3.86	5.33	15	2.71	4.4	3.48	5.01	9.55	7.29	5.31	4.31
	F45	m	6.82	3.02	4.64	7.22	4.55	5.12	3.43	4.25	2.71	5.05	9.09	4.28
		S	6.21	2.20	5.38	6.56	16.8	4.96	1.92	6.48	9.31	10.2	19.4	2.13
Slope	*UF*	m	1.78	1.67	1.69	1.61	1.67	1.83	1.78	1.8	1.51	1.58	1.57	1.69
		S	0.27	0.27	0.27	0.29	0.28	0.26	0.28	0.34	0.27	2.16	0.27	0.3
	F45	m	1.85	1.66	1.73	1.79	1.79	1.77	1.79	1.89	1.70	1.70	1.71	1.78
		S	0.35	0.29	0.26	0.25	0.32	0.26	0.32	0.29	0.30	0.28	0.25	0.22
S_{254}	*UF*	m	2.75	3.35	2.99	3.34	3.66	3.64	4.01	3.49	3.83	3.85	3.7	3.9
		S	1.08	4.07	3.56	8.15	3.87	2.33	1.15	0.56	4.32	6.14	5.11	2.15
	F45	m	2.24	2.45	3.82	3.83	3.11	3.47	3.44	3.66	3.73	3.66	3.23	3.47
		S	0.91	1.03	29.8	2.2	2.39	2.62	0.91	0.96	1.13	1.02	1.86	35
A_{254}	*UF*	m	2.75	3.35	2.99	3.34	3.66	3.64	4.01	3.49	3.83	3.85	3.7	3.9
		S	1.08	4.07	3.56	8.15	3.87	2.33	1.15	0.56	4.32	6.14	5.11	2.15
	F45	m	2.24	2.45	3.82	3.83	3.11	3.47	3.44	3.66	3.73	3.66	3.23	3.47
		S	0.91	1.03	29.8	2.2	2.39	2.62	0.91	0.96	1.13	1.02	1.86	35

3.3. Correlations between NOM and Nutrients

Spearman's rank correlation was calculated for CDOM, FDOM, Alk, Cond, pH, tot-N, NO2 + NO3, tot-P, SS, TOC and flow across all sample sites. Cross correlations were carried out to not exclude any significant correlations (**Table 10**). For the aim of this study, some of the most significant results are displayed in **Figures 10 & 11**.

FIX, BIX and HIX all correlated with each other ($p<0.001$) with a positive correlation between FIX and BIX and a negative correlation between HIX and FIX/BIX. C:T and A_{254} had a strong positive correlation with FIX and BIX and a strong negative correlation with HIX ($p>0.001$). A_{254} also correlated most strongly with TOC, while S_{254} had weak correlations with FIX, BIX and HIX while still being significant ($p<0.001$) and no correlations with TOC. E2:E3 correlated negatively with S_{254} and positively with Slope and HIX ($p<0.001$).

The correlations in **Figure 10 & 11** indicate that the correlations between OM and nutrients and abiotic factors are generally weaker than some of the correlations between different OM properties. Nitrogen did not correlate with most OM properties (**Table 11**). The strongest correlation N had was with Slope. Tot N and NO2+NO3 correlated negatively with Slope ($p<0.001$). Phosphorus correlated positively with A_{254} and negatively with HIX, E2:E3 and C:T. Suspended solids correlated negatively with HIX and E2:E3 and positively with A_{254}.

TOC correlated negatively with BIX, E2:E3 and Slope ($p<0.001$). Flow had weak yet significant correlations with C:T being positive and FIX negative. Alk, Cond and pH depending on filtering all correlated with indices ($p<0.05$) (table 1), with the strongest correlations for Alk being with A_{254} (negative) and Slope (positive). pH correlated most strongly with A_{254} (negative) and Slope (positive). The most interesting correlation for Cond for this study was with HIX, E2:E3 (positive) and S_{254}, A_{254} (negative).

Correlation plots EEM

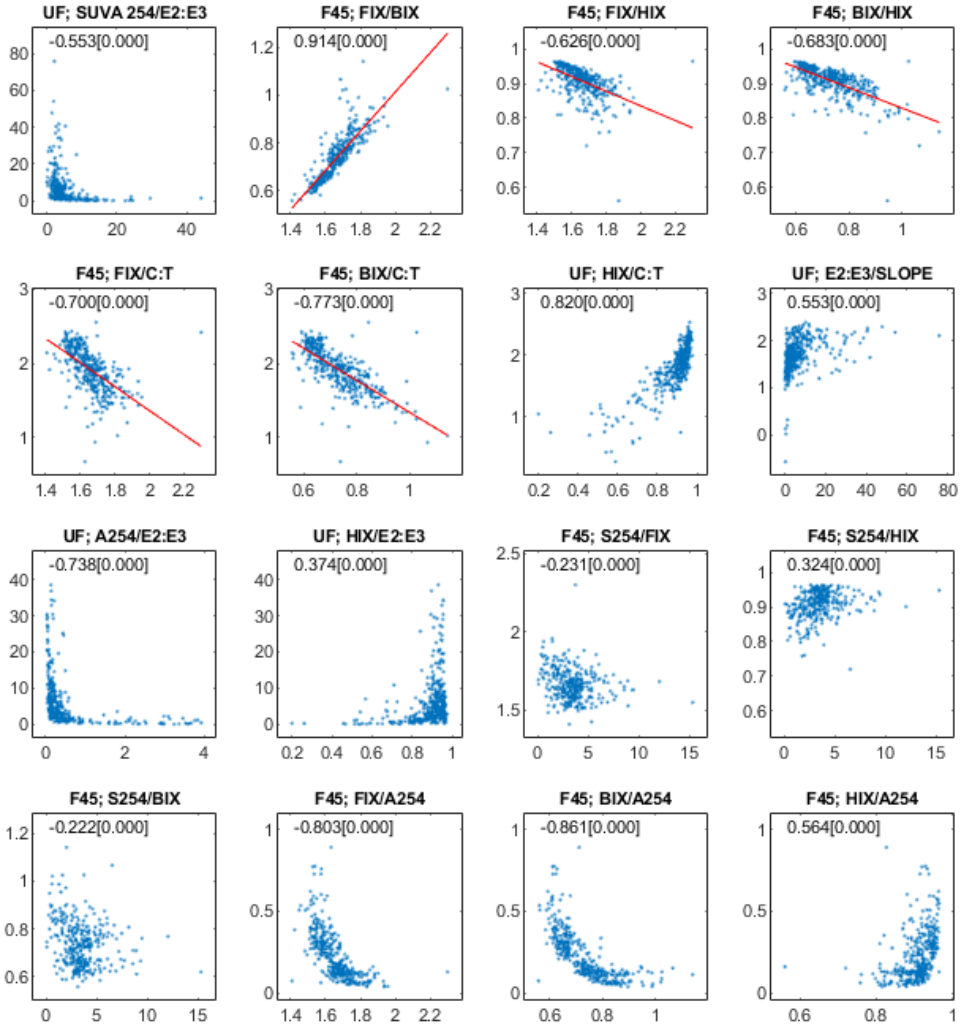


Figure 10. Correlations between fluorescence indices and absorbance indices spearman's rank correlation (ρ), brackets show significance [*p*] and are displayed in the scatter plot. Titles display filtration; first parameter in the title x-axis/second parameter y-axis.

Spearman's correlation plots

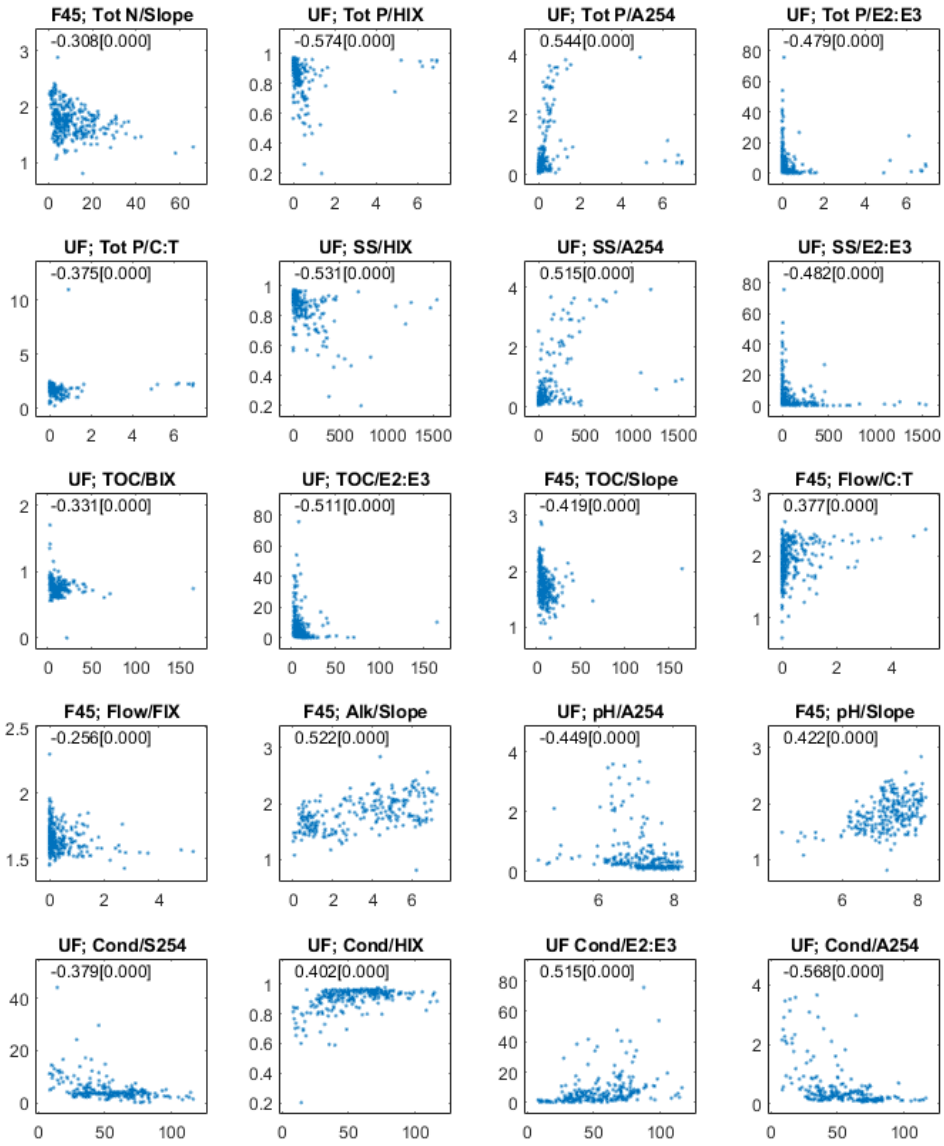


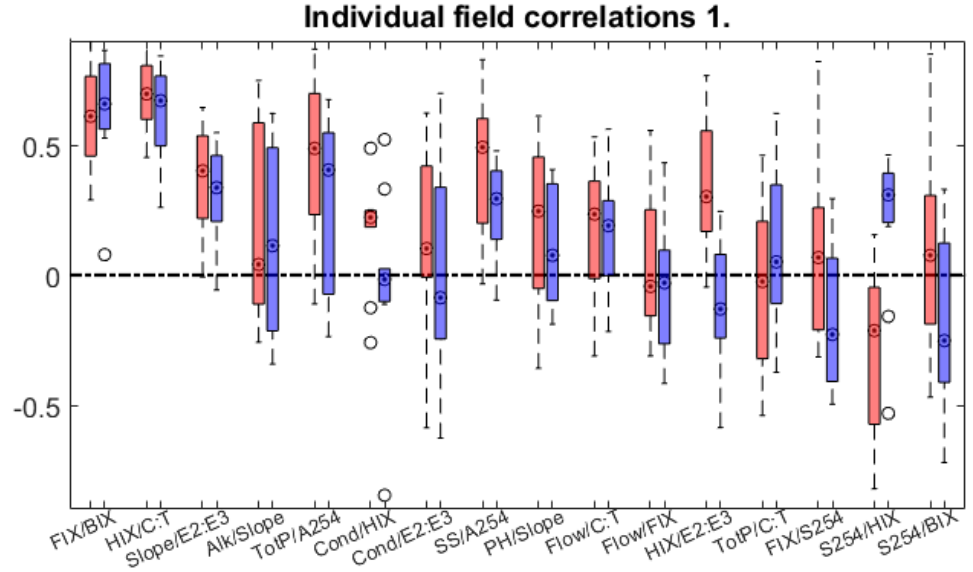
Figure 11. Titles display filtration; tot-P, tot-N SS TOC FLOW Alk pH cond and the x-axis and indices on the y-axis.

Table 10. The top right corner are *F45* samples correlations and bottom left corner are *UF* samples correlations in the table. Values with (*) are significant (p<0, 05).

	Alk	*Cond*	*pH*	*Tot N*	*NO2+3*	*Tot P*	*SS*	*TOC*	*FLOW*	*S_{254}*	*FIX*	*BIX*	*HIX*	*A_{254}*	*E2:E3*	*Slope*	*C:T*
Alk	#	0.83*	0.7*	-0.47*	-0.45*	-0.15*	-0.31*	-0.28*	-0.13*	0.13	0.23*	0.33*	0.02	-0.4*	0.14*	0.52*	-0.35*
Cond	0.82*	#	0.66*	-0.23*	-0.19*	-0.32*	-0.37*	-0.33*	-0.19*	0.12	0.24*	0.36*	0.08	-0.41*	0.2*	0.45*	-0.36*
pH	0.7*	0.65*	#	-0.21*	-0.19*	0.1	0.02	-0.18*	-0.42*	-0.01	0.24*	0.3*	0.01	-0.38*	0.12	0.42*	-0.32*
Tot N	-0.42*	-0.16*	-0.14*	#	0.99*	0.04	0.1	0.26*	0.09	0.07	0.04	-0.03	0.14*	0.1	-0.04	-0.31*	0.2*
NO2+3	-0.38*	-0.11	-0.12	0.97*	#	-0.01	0.05	0.21*	0.07	0.06	0.05	-0.01	0.15*	0.09	-0.02	-0.3*	0.19*
Tot P	-0.15*	-0.33*	0.1	0.02	-0.07	#	0.8*	0.62*	-0.14*	0.04	-0.12*	-0.16*	-0.15*	0.27*	-0.13*	-0.15*	0.02
SS	-0.33*	-0.4*	-0.03	0.06	-0.03	0.76*	#	0.59*	-0.13*	-0.01	-0.15*	-0.19*	-0.06	0.28*	-0.17*	-0.2*	0.11*
TOC	-0.29*	-0.36*	-0.21*	0.25*	0.15*	0.67*	0.61*	#	0.18*	0	-0.49*	-0.56*	0.3*	0.65*	-0.38*	-0.42*	0.49*
FLOW	-0.15*	-0.19*	-0.43*	0.12*	0.08	-0.07	-0.09	0.22*	#	-0.04	-0.26*	-0.2*	0.16*	0.12*	-0.06	-0.12*	0.37*
S_{254}	-0.36*	-0.38*	-0.3*	-0.09	-0.1*	0.17*	0.19*	0.07	0.02	#	-0.23*	-0.22*	0.33*	0.29*	0.01	0.27*	0.19*
FIX	0.15*	0.17*	0.18*	0.09	0.07	0.02	0.05	-0.28*	-0.2*	-0.25*	#	0.91*	-0.63*	-0.8*	0.46*	0.38*	-0.7*
BIX	0.18*	0.19*	0.23*	0.02	0.01	0.02	0.04	-0.33*	-0.17*	-0.21*	0.88*	#	-0.68*	-0.86*	0.51*	0.44*	-0.77*
HIX	0.36*	0.4*	0.14*	0.01	0.06	-0.57*	-0.53*	-0.18*	0.15*	-0.25*	-0.41*	-0.52*	#	0.57*	-0.3*	-0.17*	0.76*
A_{254}	-0.52*	-0.57*	-0.45*	0.11*	0.05	0.54*	0.52*	0.73*	0.21*	0.65*	-0.46*	-0.48*	-0.23*	#	-0.54*	-0.51*	0.66*
E2:E3	0.42*	0.52*	0.31*	-0.04	0.02	-0.48*	-0.48*	-0.51*	-0.08	-0.55*	0.24*	0.21*	0.38*	-0.73*	#	0.46*	-0.35*
Slope	0.49*	0.43*	0.41*	-0.3*	-0.26*	-0.23*	-0.24*	-0.44*	-0.15*	-0.28*	0.16*	0.19*	0.26*	-0.54*	0.54*	#	-0.37*
C:T	0.06	0.05	-0.13*	0.1	0.12*	-0.38*	-0.36*	0.09	0.32*	-0.16*	-0.58*	-0.72*	0.82*	0.06	0.16*	0.04	#

Figures 12-13 show the distribution of correlations between observation fields and the underlying corresponding table shows the significance of the distribution. Cond, Alk and pH for observation fields 21E and 7E, and S_{254} for observation field 14AC are not displayed in **Figure 12-13** due to insufficient data. Correlation tables for each observation field can be found in **Appendix 2.**

FIX/BIX, and HIX/C:T had positive correlations that are significant in most observation fields. Positive correlations between Slope/E2E3, Tot P/A_{254} and SS/A_{254} and mostly positive correlations between Alk/Slope flow/C:T were observed (**Figure 12**). Split results regarding *UF* and *F45* samples were observed in the correlations between pH/Slope and HIX/E2:E3, with the *UF* samples showing several significant positive correlations while there were no conclusive results for the *F45* samples. Correlations between S_{254}/HIX show a reverse pattern with *UF* samples correlating negatively and *F45* correlating positively. No conclusive results for observation fields could be found for the correlations of Cond/HIX, Cond/E2:E3, Flow/FIX, Tot P/C:T, FIX/S_{254} and S_{254}/BIX.



UF	+10	+12	+7	+4	+7	+1	4	+7	+4	+3	3	+6	3	+1	-4	4
F45	+11	+10	+6	+3	+6	3	3	+2	0	+2	2	2	3	-1	+2	4

Figure 12. Distribution of spearman's ρ for twelve observation fields with the number of significant correlations in the table below. Table (+) meaning only positive, (-) only negative and (blank) meaning mixed positive and negative significance. I.e. FIX/BIX have 10; *UF* observed positive correlations and 11; *F45* positive correlations that are significant (p<0.05).

BIX had a negative correlation with C:T and HIX in a strong majority of the observation fields, while correlations between pH/A_{254}, TOC/slope and FIX/C:T had negative correlations in most of the observation fields with only significant negative correlations being observed (**Figure 13**).TOC/BIX had mostly negative correlations with one *UF* outlier showing a significant positive correlation. S_{254}/E2:E3 showed a split result with the *F45* samples showing no correlation and *UF* samples showing a strong negative correlation for almost all observation fields. Tot P/HIX showed the same pattern with strong negative correlations for *UF* and no conclusive results for *F45*. Tot P/E2:E3 and SS/E2:E3 had negative correlations with *UF* samples but no correlations for *F45*. Following correlations showed no conclusive results: Tot N/slope, Tot P/slope, SS/HIX, Cond/S_{254}, TOC/E2:E3 and Cond/A_{254}.

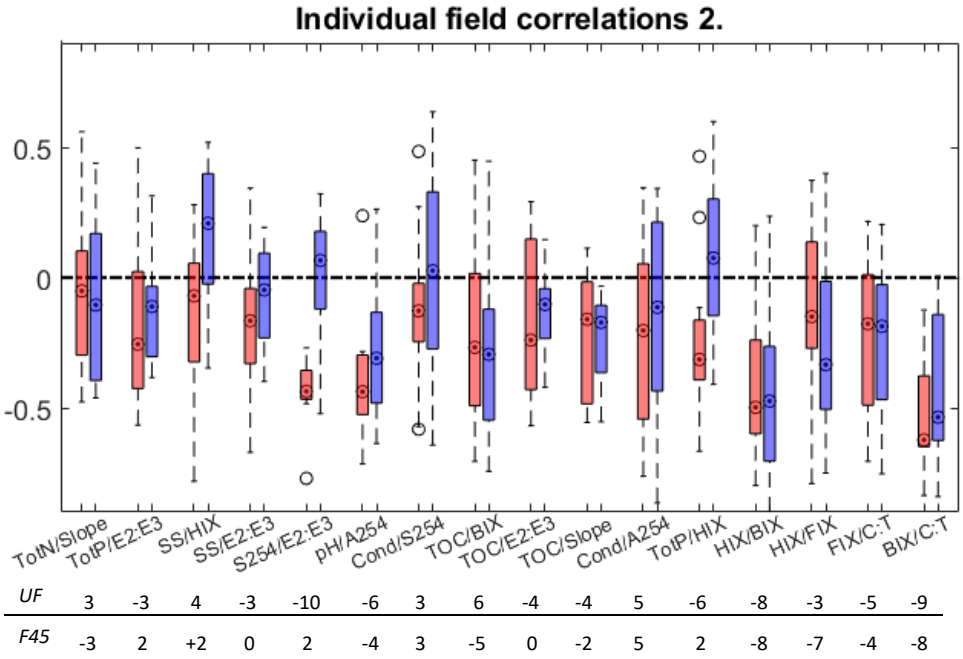


Figure 13. Distribution of spearman's ρ for twelve observation fields with the number of significant correlations in the table below. Table 3. (+) meaning only positive, (-) only negative and (blank) meaning mixed positive and negative significance (p<0.05).

4. Discussion

The results of two years of monitoring the quantity and quality of NOM and nutrient leaching from 12 observation fields will be discussed in this chapter. The discussion will be focusing on the mechanisms behind the observed results including the spatiotemporal differences and the linkages between NOM, nutrient and abiotic factors. The effects of the sample processing, including filtering and the interferences from different parameters will also be discussed. Finally, the results will be interpreted with regards to the effect that FDOM has on the quality of water bodies. When discussing the results, it is assumed that the results for the filtered samples represent DOM properties and that comparing unfiltered and filtered sample results infers information about properties of POM.

4.1. Spatial controls of fluorescence and absorbance indices

The results showed that parameters that control the quality (FIX, BIX, HIX and C:T) of FDOM included (1.) soil texture and the sloping angle of the field, and (2.) precipitation and runoff, while the impact of fertilization and agricultural practices on FDOM and CDOM were harder to determine.
Clay soils and loam soils had different patterns for leaching of FDOM. The leaching of FDOM from clay soils was more microbial (BIX) and freshly produced (FIX) with noticeable differences between DOM and POM, while loam soils had higher leaching of terrestrial humified material (HIX). These conclusions are supported by Kalbitz *et al.,* (2000), who found that hydrological conditions were more influential than biological conditions when it comes to leaching of NOM in field conditions.

Clay soils have a higher absorption capacity that inhibits fast degradation of FDOM (Singh, 2016). The reason for the slower degradation rate is the reduced availability of microorganisms to access the FDOM when absorbed onto soil particles (Kalbitz *et al.,* 2005). Soils with fine texture are however more prone to water erosion, especially sloping soils, which are more likely to lose high quantities of NOM due to increased absorption to small soil particles (Munn 1973). The parameters controlling the size and aromaticity (E2:E3, SLOPE and S_{254}) of CDOM showed no clear pattern between spatial controls for the observation fields. There was however a tendency for loam

soils to have CDOM with lower MWS, while no credible difference for aromaticity was observed. The DOM showed no significant spatial difference for S_{254F45}, indicating that the aromaticity of the CDOM flowing from the observation fields was homogenous and not affected by spatial controls. The variance between Observation fields depending on the quality of the NOM can be divided into three groups that will be discussed in detail below; 2M, 12N and 14AC was dominated by terrestrial hemic NOM and high precipitation; 21E and 20E had higher input from microbial sources and low precipitation; 1D and 11M had significant differences between POM and DOM, with POM indicating higher microbial origin.

Impact of wet weather conditions on course soils

Observation fields 2M, 12N and 14AC had coarse soils with the highest total discharge and the highest amounts of terrestrial humified FDOM (HIX & C/T). Observation fields 2M and 12N were both located in the same production area and had fairly similar soil texture of loam and sandy loam. They also had high precipitation (631 mm and 684 mm respectively) and a high medium temperature of 7.8 °C. They differed in cropping pattern and fertilizing treatment; 2M had planted ley seeds and winter wheat while 12N was planted with potato and grain. 12N was treated with sludge while 2M was left unfertilized. There was also a large difference in area 2M, which was twice the size to that of 12N. The differences between 2M-12N and 14AC were however more pronounced, with 14AC having a much colder climate 2.7°C and lower precipitation 541 mm. However, compared to the other observation fields, 14AC still had relatively high precipitation. 14AC (8.4 ha) was also smaller in size than that of 2M-12N and had a lower sloping terrain. Even though 2M-12N and 14AC had different forms of loam, they all had a low clay fraction. 2M-12N had very similar flow rate patterns (**Figure 1**) where the flow spiked after rain events and then slowly subsided, while flow rates for 14AC spiked after rain events and then quickly subsided. The warm climate conditions and high precipitation and runoff for 2M-12N may explain the high transportation of humified allochthonous NOM indicated by the HIX and C:T ratio, as the low clay fraction, high temperature and precipitation play a key role in the fast degradation of OM (Campo, 2019; Singh *et al.*, 2016; Jones & Edwards, 1998). The high flow rates could then transport the humified FDOM at fast rates. The source and freshness of the FDOM in 2M-12N and 14AC were very similar and came from terrestrial sources. However the humification of the NOM in 14AC was slower than for 2M-12N, which could be explained by the colder climate for 14AC, where lower temperature and solar radiation affected the biodegradation and decreased the humification of OM (Campo, 2019).

Effects of dry weather conditions on soils

21E (loam) and 20E (clay) were observation fields with vastly different soil textures but shared the same production area, average temperature 6°C and low precipitation (21E 518mm and 20E 475mm). Both soils had higher amounts of freshly produced microbial material (BIX & FIX) flowing from the observation fields. 21E and 20E were also small observation fields and had the lowest discharge rate in total and in proportion to the precipitation (21E discharge 94 mm (18%) and 20E 72mm (15%)). Both observation fields had longer dry periods followed by flow spikes that quickly subsided during winter and spring. This indicates that runoff only occurred after heavy rainfall and most of the water were lost through evapotranspiration. Shi & Schulin, (2019) showed that there is an increase in FIX from surface runoff right after rainfall in agricultural fields. Microbial degradation of organic material is reduced during dry conditions, which limits the activity of microorganisms and leads to an accumulation of more easily degradable substances (Marschner & Kalbitz, 2003). When soils are rewetted there is a shift within the microbial community, stimulated by the availability of easily degradable substances, which results in leaching of higher amounts of labile OM *(*(Marschner & Kalbitz, 2003; Vujinovic *et al.*, 2019).

Fine textured soils and sensitivity to water erosion

Observation fields 1D, 11M and 7E were all glacial clay soils but shared different flow patterns and leachate composition; 1D and 7E had similar flow patterns, while 1D and 11M had leachate compositions containing high amounts of SS and P indicating erosion (Soinne *et al.*, 2016). Both observation fields 1D and 11M had TOC levels that were directly connected to the SS of the leachate. On a closer look, 1D had a pattern of more consistently high leaching of TOC and SS, while 11M had high TOC and SS levels connected to flow spikes (**Figure 1**). The NOM flowing from 1D mostly came from terrestrial sources but differed significantly regarding filtering in regards to source, degradation, MW and aromaticity. Observation field 11M had similar results regarding the effects of filtering but was not significant to the same extent. The POM in 1D and 11M had a high MW and was of a microbial origin, with high amounts of the tryptophan-like fluorescence. The DOM indicated a lower MW and was more terrestrial. These findings suggest that soil particles and labile POM were continuously leaching from 1D, while erosion in 11M was limited to periods of high flows when TOC and SS increased sharply. Aggregation of mineral particles are a curtail part for the stability of clay soils. Ca^{2+} and soil organic matter are main enhancers of soil aggregate formation and helps stabilize the soil, making it more resisted to erosion (Singh *et al.*, 2016; Bronick & Lal 2005; Soinne *et al.*, 2016). Glacial soils often have a poorer aggregate structure due to the lower amount of organic matter and calk in the soil. The soil organic

matter content was not investigated in this study however, parameters such as SS, P and information on glacial and post glacial soils indicate poorer structure of 1D and 11M. High flow events are connected to increases in erosion where soil particles are flushed into the water stream, leading to elevated concentration of SS and terrestrial DOM (Hur *et al.,* 2007). This may indicate that the microbial and tryptophan NOM had formed complexes with the soluble particles that were abundant in 1D and 11M.

Finer textured soils have a higher specific surface and subsequently higher adsorption capacity for DOC (Singh, 2016). Where DOC and soil particles or minerals form organo-mineral complexes, these complexes are formed by the adsorption of DOM onto soil particles and are more resistant to degradation than free DOC (Bolan *et al.,* 2011). Organic adsorbed mineral complexes might appear as DOM with large MW distorting the results in the absorbance indices (Bolan, 2011; Hansen, 2016). The formation of larger soil organic colloids could then explain the removal of microbial NOM that should have no problem passing through the filter in observation fields with high clay content (**Figure 4**).

Samples discrepancies

Sampling varied greatly between observation fields and ranged between 15-52 samples. Discrepancies in collection of samples could have affected the spatial results discussed in this section.

4.2. Seasonal variation of NOM and nutrients

The location of the observations fields extended from the most southern coast to the northern inland of Sweden, covering a range of different climatic and weather conditions. Soil texture and the physical conditions of each specific observation field also played a major role in the diversity of quantity and quality of the NOM. The spatial controls are reflected in the wide range of results for each month and make it difficult to deduce significant differences between the different months. Combining results from all observation fields nevertheless gives a broad picture of the temporal dynamics of FDOM. Because of the low affinity of significant differences, this part will be more speculative with an objective of understanding the overall seasonal patterns for the FDOM and CDOM (**Figures 6-8**). The most notable seasonal variation for FDOM and CDOM indices was during autumn in the month of NOV when some fluorescence indices shifted rapidly. Nutrients, TOC and flow rates had patterns that fit with FDOM and CDOM indices (**Figure 9**).

FIX and BIX indices shared similar seasonal distributions. FIX/BIX were higher during spring and the beginning of summer. The proportion of microbial-freshly produced material gradually decreased from summer until the end of autumn, with NOV marking a turnover of the composition of NOM. The opposite was observed for HIX where values were lower during winter and spring, with a gradual increase from the beginning of the summer until the middle of autumn and then a rapid decrease in NOV.

The C:T ratio had a more stable seasonal pattern compared to other fluorescence indices. C:T ratio were more tryptophan dominated during the first half of the year (**Figure 7**).

The seasonal change in MW fluctuated most in autumn. E2: E3 fluctuated at the beginning of the year but became more stable during summer, while Slope had a more even pattern during spring and summer with a slow increase until AUG.

The similarity in results for fluorescence indices between *UF* and *F45* samples during the summer months indicates a lower input of POM, with a visible distinction of content between POM and DOM during autumn and winter. Microbial autochthonous and MW POM peaked in the month of NOV indicating microbial adsorption onto mineral surfaces. While POM had a sharp peak followed by a quick decline, DOM had a steady increase of microbial material during OCT-DEC.

The change in composition of NOM and MW most likely comes from a change in climate and weather during NOV towards wetter conditions, as well as agricultural practices applied months before. Harvesting, plowing and cultivating predominantly occurred during AUG-OCT, with an increase in precipitation during late autumn and winter (Norberg *et al*., 2017). The increase in precipitation was visible in the increase in flow and leaching of nutrients in NOV (**Figure 9**). Tang *et al.,* (2020) found a shift in the composition of FDOM during wet seasons towards more freshly produced OM.

The removal of plants and the turnover of soil shift the microbial community in the soil and enhance the degradation of more accessible OM (Six *et al.*, 2004). Rewetting and surface runoff created by initial precipitation have been found to increase the autochthonous-microbial material leaching from agricultural fields *(*Vujinovi, *et al. 2019;* Shi & Schulin, 2019). The increase of MW in NOV was most likely caused by an increase in SS. The removal of crops and the turnover of soils combined with the increased runoff during NOV increased the amount of erosion and SS entering the stream.

4.3. Interferences of SS and N on fluorescence and absorbance indices

The accuracy of the *UF* and *F45* samples will be debated in this section. Temperature, pH and inorganic particles affect the reliability of the fluorescence and absorbance indices (Weishaar *et al.,* 2003; Hudson *et al.,* 2007). All samples were analysed under lab conditions after being cooled to 8 °C until analysed. The pH of most observation fields was around neutral with the exception of 14AC (pH 5). Filtering eliminates possible disturbance from soluble particles in the samples and gives clearer results, but might also remove DOM from the solution, thus giving incomplete results. DOM is able to pass through a pore sized of 0.45 µm (Bolan *et al.,* 2011). The concentration of TOC *UF* was significantly ($p = 0.02$) higher than the DOC in *F45* samples indicating that filtering process indeed removed particles adsorbed NOM. The filtering of the 0.45 µm membrane might also retract the OM adsorbed by soluble particles. There are also inorganic particles that may distort the results of absorbance and fluorescence indices since they are not removed by filtering.

A_{254}, S_{254} and E2:E3 function within the UV/Vis-spectrum and can be affected by dissolved inorganic particles present in the water. Soluble solids, iron ions and nitrate absorb and scatter the light near and at the wavelength 254 nm, which may significantly disturb the results (Weishaar *et al.,* 2003; Sgroi *et al.,* 2020). This implicates some of the results for the *UF* which had a much higher concentration of SS than *F45* samples for CDOM. Nitrate can however penetrate the filtering process when not adsorbed and distort the results even in the *F45* samples. The results from $1D_{UF}$ and $11M_{UF}$ (clay soils) are especially subject to scrutiny with high values in SS and significantly different results for E2:E3, S_{254} and A_{254} between *UF* and *F45* samples. Observation field $14AC_{UF}$ had a low SS and nitrate leaching from the field, with significant differences between *UF* and *F45* samples for the S_{254} indicating that the material removed in the filtering process might be more aromatic CDOM. The low pH in 14AC could affect the results for S_{254} but it does not explain the significant difference in aromaticity between *UF* and *F45* samples. Fluorescence indices also have a tendency to under report at low pH as in 14AC. Lower pH can cause the organic molecule to curl, decreasing the fluorescence signature (Hudson *et al.,* 2007). 14AC was the northernmost observation field and could have input from sources outside the observation field that might explain the difference in aromaticity between $14AC_{UF}$ and $14AC_{F45}$. The spectral Slope works within the same UV/Vis-spectrum as the A_{254}, S_{254} and E2:E3 indices but showed no significant difference between *UF* and *F45* in this study. The reason behind this is uncertain. The overall trend was however that the *UF* had higher MW (E2:E3 and Slope) than *F45* samples.

The effects of SS on the accuracy of FDOM are disputed as the effect differs between various studies. For example, there was a difference between the *UF* and *F45* samples regarding the fluorescence indices and it is not only limited to the soils with high SS, which indicates that there might be a difference between the quality of DOC, TOC and AOC. Fluorescence indices can be affected by SS but *UF* samples still offer a representation of FDOM that is important to investigate. The problem with SS is the increasing disturbance for the primary inner-filter effects in the curette. Fluorescence data in this study was corrected to account for the inner-filter effects according to (Ohon, 2002)

Some parts of the florescence can however be affected by SS. According to Lee & Ahn (2004); Hur (2007 & 2008); McKnight *et al.,* (2001) the effect of SS on florescence indices are negligible as they found no difference in correlation FDOM and biochemical oxygen demand BOD between treated and untreated samples. On the other hand, Sgroi *et al.,* (2020); Baker & Inverarity (2004) showed significantly better results for FDOM in the tryptophan range of the spectrum when removing SS in the water by filtering. However, the humic range of the FDOM showed no significant difference between unfiltered and filtered samples (Sgroi *et al.,* 2020). FDOM and adsorption to SS surfaces

4.4. Mineral adsorption of microbial matter and aggregation of humic matter

This section will discuss the content and formation of POM and why results differ between POM and DOM. The results indicate that there was a significant difference in quantity of DOC and TOC and quality DOM and POM for loam and clay soils. The microbial matter was less inclined to pass through the 0.45 μm membrane than to that of more humified material in clay soils 1D and 11M. In contrast, the loam soils 16Z and 21E indicate that humified matter was able to pass the 0.45 μm membrane to a higher extent than that of less humified material. The differences of between POM and DOM in 11M and 21E were visible but not significant. The difference between TOC and DOC were visible but not significant for any single observation field due to the low sample size, while there was a significant difference when combining all samples ($p = 0.02$).

FDOM adsorbed onto mineral surfaces has a different character of fluorescence with adsorbed OM emitting light of a lower energy level (longer wavelength), indicating adoption of more autochthonous microbial material onto inorganic suspended particles (Postnikova 2015). Hu *et al.*, (2019) compared the Suspended POM between two different rivers and found that the river that contained more SS also had more autochthonous

microbial NOM adsorbed onto the surfaces of inorganic particles, which is similar to values observed in this study. The accessibility of adsorbed NOM for microbes differs between environments. The soil environment, soil DOM adsorbed to the surface of particles, mineral and aggregates are less available for microorganisms than DOM in the aquatic phase of the soil (Kalbitz *et al.*, 2005; Six 2004). This dynamic changes when OM adsorbed to soluble particles enters an aquatic environment, for example a drainage ditch, which renders the adsorbed POM accessible for microbes (Postnikova 2015).

The binding of DOM to SS is dependent on the electrostatic charge of the mineral surface and the surface of the DOM. The adsorption of DOM onto the mineral surface is at its strongest when the mineral surface is positively charged and the DOM is negatively charged (Fein, 1999; Liu & Gonzalez 1999). This electrostatic charge is in turn dependent on the pH of the soil solution, where higher pH results in lower adsorption of DOM (Swenson, 2015; Liu & Gonzalez, 1999). According to Banaitis *et al.,* (2006) humic substances are more prone to adsorption compared to microbial material under lower pH (pH 5.5). The microbial metabolites and humic substances of soil solutions both have pH dependent charges where the adsorption potential decreases with rising pH. However, the adsorption dependent charge of humic DOM seems to be more sensitive to pH than microbial DOM, where the negative charge of humic acids starts to rapidly decrease at pH 6.0 while some microbial metabolites still regain their negative charge at pH 6.8 (Majzik & Tombácz, 2007; Swenson, 2015). The soil pH of most observation fields in this study was however at a neutral to high pH and the adsorption of different DOM were probably more dependent on other parameters in the soil solution.

The separation of humified and microbial material in DOM and POM could be caused by the difference in P content in microbial metabolites and the Ca^{2+} ion concentration in clay and loam soil. The orders of Ca^{2+} ion concentrations of soil solutions were much higher in 16Z and 21E compared to 1D and 11M (data not showed). Majzik & Tombácz, (2007) found that Ca^{2+} ions can act as a bridge between humified DOM and the mineral surfaces, where an increase in the Ca^{2+} ion concentration increases the amount of humic acids adsorbed to soil minerals substantially. Majzik & Tombácz, (2007) also found that the increase in Ca^{2+} ions resulted in adsorption of more humified DOM while leaving less humified DOM in the aquatic phase. The Ca^{2+} ions also function as a bridge between humic substances and cause aggregation of humic molecules, which increases the humic fraction in POM (Kloster *et al.,* 2013).

In contrast, the tot-P concentrations were reversed; 1D and 11M had high concentrations while 16Z and 21E had low concentrations of tot-P (**Table 8**). Microbial metabolites containing phosphate had a greater attraction to mineral surfaces than that of other microbial metabolites (Swenson T, L, *et al.*, 2015). The proportion of organic-P was not measured in this study, but organic-P account for >50% of tot-P in agricultural fields (Stutter *et al.*, 2012). Tot-P was linked to TOC for 1D and 11M and tot-P had significant correlations with all fractions of FDOM in 1D, which might indicate that the presence of microbial metabolites with higher P content resulted in higher adsorption.

1D and 11M had a 40-55% reduction of organic carbon between TOC and DOC (data not showed). The high SS and MW indicate that the POM was composed of autochthonous microbial NOM likely adsorbed onto the surfaces of inorganic particles, while DOC were composed of more allochthonous terrestrial DOM (**Figure 14**). The results for 16Z and 21E indicate that POM was more humified while no difference in origin was observed for POM and DOC. The high Ca^{2+} ion concentration and low SS indicate that the POM was likely aggregated humic substances coagulated by Ca^{2+} ions (**Figure 14**). No indication of higher aromaticity was detected while the MW was low.

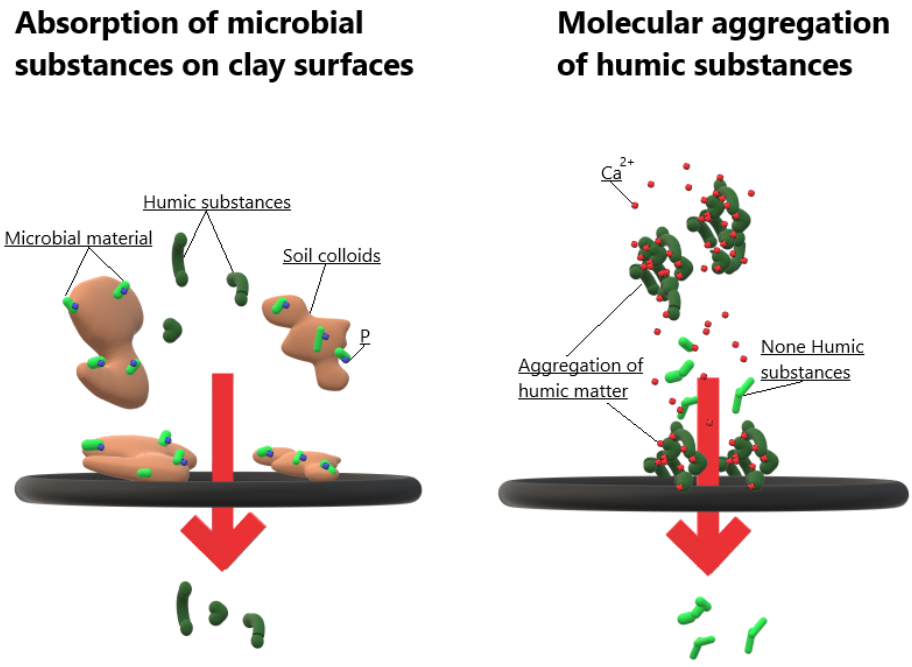


Figure 14. Visualizations of the removal of microbial metabolites adsorbed onto mineral surfaces and humic aggregates removed by filtering through a 0.45 µm membrane separating POM and DOM depending on interactions with Ca^{2+} or adsorption by SS in the solution.

The conclusions made in this section need further analysis to distinguish true results from measurement errors that can be caused by SS. One way to do this is to detach adsorbed OM from the SS and then analyse the separated FDOM and CDOM. The method of detaching adsorbed OM can be done as described by Hu *et al.*, (2019), namely that after filtration, SS is collected and then freeze-dried before being diluted with acids and then centrifuged. After this, the solution is re-filtered and the remaining filtrates are analysed.

4.5. Links between origin, degradation and complexity of NOM

This section will be focusing on the overall and the observation specific correlations between FDOM, aromaticity and MW. Due to many correlations being significant, only correlations (ρ)>0.3 or those that have more than three observation specific correlations will be considered relevant. Many of the correlations found between FDOM in the study were in alignment with previous research. The correlations between MW and humification were significantly affected by filtering with the DOM having positive correlations and the POM having negative correlations. The S_{254} had few significant correlations and was mostly unaffected by other parameters.

Interactions between FDOM

Correlations between EEM indices in Swedish arable fields showed that the source, transport and degradation of DOM were all correlated. The rate of freshness and microbial produced DOM and POM were directly linked. This phenomenon was significant in almost all observation fields as a persistent positive correlation between FIX and BIX (**Figure 12**). The FDOM produced by microbial sources are released from cell lyses and are of lower aromatic structure (McKnight *et al.*, 2001), like lipids proteins and amino sugars that are quickly utilised by other fast growing microorganisms and subsequently leave the soil as CO_2 through microbial respiration (Garcia-Pausas & Paterson, 2011). The microbial produced matter will therefore not stay in the soil for long, linking the freshness directly to the source of the OM. HIX correlated inversely with FIX and BIX indicating that more humified organic material was connected to higher input from terrestrial allochthonous sources. This correlation was observed in most observation fields and was stronger in DOM than POM (**Figure 12**). The correlation is supported by Songyan, (2019). The humification rate was not as dependent as the origin and freshness relationship. Terrestrial matter is more recalcitrant and can be humified to a higher extent by biological and physical processes, such as soil moisture, temperature and solar radiation, which enhance the humification process (Campo, 2019; Lehmann, 2006).

The C:T ratio was negatively correlated with FIX and BIX and positively correlated to HIX (**Table 10**). The correlation between HIX and C:T was significant for all observation fields (**Figure 12**) indicating that the C:T ratio was tracing the same organic molecules as HIX. The C:T and BIX/FIX correlations were significant in most of the observation fields indicating the same dynamic as for the HIX to BIX/FIX indices, where the decrees in tryptophan and amino acid were linked to the humification rate (**Figure 13**). This is because tryptophan may be present in long transported microbial DOM if environmental factors (low temperature, mineral adsorption or drought) inhibit the degradation of the more easily degradable molecules (Liu *et al.,* 2019 and Yuste, 2007).

Interactions between CDOM

The overall correlation between E2:E3 and Slope was lower than what could be expected when both ratios are tracking MW and are working within the UV/Vis-spectrum (**Table 10**). E2:E3$_{UF}$ had an inverted correlation with S_{254UF} however no correlation could be found in the *F45* samples. The correlation between MW and aromaticity was observed in a majority of observation fields for POM but not for DOM. This phenomenon might be explained by the removal of heavy, highly aromatic POM through the filtering process that disjoints the correlation. Mouloubou, O,R, *et al,*. (2015) found that washing samples with Sodium hydroxide and subsequently removing NOM with high MW detached the correlation between E2:E3 and S_{254}.

Correlations between absorbance indices and fluorescence indices

In several of the observation fields, E2:E3$_{F45}$ and Slope$_{F45}$ had significant correlations with freshness and origin of NOM BIX$_{F45}$ and FIX$_{F45}$ (**Figure 11**). Previous studies have shown that DOM with microbial origin has a lower MW (Sgroi *et al.,* 2020; Shi & Schulin, 2019), while a weaker correlation has been observed for POM.

The correlation between humification (HIX, C:T), aromaticity and MW (E2:E3, Slope, S_{254}) was weak yet significant, and had opposite correlations depending on filtering (**Table 10**). Humification increased with lower MW and aromaticity for POM, while the reversed was observed for DOM. Previous studies have found that humification correlated with higher aromaticity and MW, which runs contrary to the results of the POM while being in line with results from the DOM (Peuravuori & Pihlaja, 1997; Weishaar *et al.,* 2003). The differences in correlation between POM and DOM could be caused by the interference of SS on the UV-vis absorbance spectrum in the *UF* samples and the adsorption of more microbial matter to

SS in some clay soils. Correlation between SS and $E2:E3_{UF}$ indicates that more suspended materials increases the MW. Therefore, the removal of SS might better represent the true interaction between MW and humification.

4.6. Interactions of fluorescence and absorbance indices, nutrients and abiotic factors

The correlations between nutrients and FDOM were poor with the exception of HIX_{UF} and tot-P. Tot-N had negative and positive correlations with FIX and BIX for several observation fields. The reason behind this pattern was unclear but could be connected to application of manure and mineralization. The leaching of N and P was investigated field specifically and temporally over the same period that FDOM data was collected. The relations between the leaching of N, P and the qualities of FDOM were examined with spearman's correlation (ρ)>0.3 for all samples and specifically for each observation field (**Figure 12**).

Connections between Tot-N, FDOM and CDOM

No overall correlations were found between the loss of total-N, NO_2/NO_3 and any of the FDOM indices; however, both positive and negative correlations were found for several of the specific observation fields. Total-N had a weak reversed correlation with the Slope and a fair reversed correlation with Alk. The influence that N had on Alk has been known for a long time, with Taras, (1950) showing that a decrease in Alk leads to a higher leaching of nitrogen. The DOM correlation between tot-N, NO_2/NO_3 and Slope was significant with only a few observation fields exhibiting a significant negative correlation, which indicates that higher concentration of N was connected to CDOM with higher MW. The correlation in **Table 10** indicates no linkage between tot-N and FDOM. There were however several significant correlations between tot-N, FIX and BIX for specific observation fields (**Appendix 2**). The linkage was unclear but seems to be connected to the application of manure (**Table 3**). Observation fields with low or no application of manure had negative to no correlation between tot-N, FIX and BIX, while observation fields with high application of manure in general had positive correlations. This suggests that the application of manure and the leaching of N and autochthonous microbial matter are connected. Nett *et al.*, (2010) found that long-term addition of organic-N increases the microbial activity in the soil. The application of organic-N and urea (NH_4) enhances mineralization, converting organic-N into NO_2/NO_3. However the linkage between application of manure, mineralization, tot-N and microbial activity also depends on the drainage capacity of the soil as well as environmental factors such as moisture, temperature and the type of manure applied (Van

Es H. M *et al.*, 2006; Nett *et al.*, 2010). This suggests that the correlation between leaching of N, FIX and BIX were dependent on the immobilization or mineralization status of the soil.

95% of the total-N consists of mineralized NO_2^-/NO_3^- that are more mobile and sensitive to leaching than that of organic-N (Van Es H. M *et al.*, 2006). An earlier study found that the activity of the enzyme peroxidase, which breaks down larger organic structures into simpler organic substances in agricultural soil, was negatively correlated with the proportion of reduced sugar and positively correlated with the mineralization of N (Tian L, 2010). This may explain why larger organic molecules were correlated to the proportion of mineralized N in the soil (correlation Slope and tot-N), where easily degraded molecules (sugar or amino acids) slow down the mineralization rate of N. These easily degradable organic molecules could be represented by the FIX and BIX indices, which correlated with the Slope ratio. There was however no correlation between FIX/BIX and N or between N and E2:E3 or S_{254}. The contradicting results regarding the correlation between MW and N might indicate that nitrogen was mostly controlled by different factors and dynamics than those that control the quantity and quality of FDOM.

The observation fields that had the highest total-N losses when FDOM samples were collected are 21E, 12N and 4O (mg/l). However, looking at the overall leaching proportional to the size of the arable field, 12N had three times the leaching of nitrogen (198,7 kg/ha) (Norberg *et al*., 2017,2018 & 2019). Observation field 12N had a coarse soil texture of sandy loam and was treated with Sludge (biogas). All observation fields were treated with some sort of slurry except for 21E, 6E, 2M, 4O and 5O. According to Johnsson & Hoffman (1996 &1998), soils that had liquid slurry applied to them had higher nitrogen losses than those of mineral fertilizer, and soil with coarser texture exacerbated higher N losses. The quantity and timing of the application of N fertilization are also of importance regarding leaching, where an over application of liquid fertilizer is a main cause of leaching (Thornsen, 1993).

Connections between Tot-P, FDOM and CDOM

There were some correlations between the leaching of tot-P and the quality of DOM. Higher tot-P leaching was linked to less humified matter and to the quantity of SS and TOC, with the observation fields that experienced the highest leaching of P (1D and 11M) also having the highest losses of SS and TOC. Therefore, the retention of NOM and humification are important steps in the retention of tot-P. The relation between erosion and leaching of tot-P are closely linked; Munn (1973) showed a strong positive correlation

between leaching of P and erosion where soils with finer texture were more sensitive to losses of absorbed P, especially for soils with a steep physical slope. The connection between humification and leaching of P in this study was reversed with an increase in P losses resulting in lower amounts of humic matter indicated by HIX and C:T (**Figure 12 & 13**). However the correlation between tot-P and humification was only observed for POM with an overall negative correlation. This might be caused by humic substances and P competing for the same adsorption surfaces of goethite where humic acids had reduced adsorption with increasing pH (Antelo *et al.,* 2007), which might explain why tryptophan had a higher affinity for adsorption compared to humic substances in this study. The pH was high in most observation fields, ranging from 6.5-7.9, except for 14AC which had a pH value of 5. There was also a correlation between E2:E3 and tot-P, however no correlations could be found for S_{254} or spectral Slope. This might indicate that tot-P was connected to the MW of NOM but the correlation between E2:E3 and tot-P could also be found for E2:E3 and SS. No correlations were seen for P in the DOM fraction, reaffirming that the main source controlling the losses of tot-P are connected to soluble particles POM larger than 0.45 um.

Flow impacts on FDOM

Several studies have shown the effects that the drying and rewetting of soils have on the quantity and quality of OM, but this was however not observed for the correlations in this study. During the dry period there is acumination of dead root and microbial material in the soil which rapidly starts to degrade during rewetting, where physical processes and increased microbial activity release nutrients and organic material (Bottner 1985; Kieft *et al.,* 1987). After the rewetting there is an increase of tryptophan and a release of simpler organic materials resulting in a decrease in S_{254} (Lebuhn, 1994; Vujinovi´c, 2019). Correlations between flow and other parameters were overall low with the only correlation being significant for C:T ratio where higher flow indicates an increase in the leaching of more humic matter, which is in line with Carstea *et al.,* (2010). There was no correlation however regarding MW or aromaticity to flow. As previously mentioned, the sampling was made with an interval of two weeks or when water in the ditches was available. The broader monitoring conducted in this study was not able to track fast changes caused by rain and initial runoff from rewetted soils, which might have the most influence on the composition and quantity of the DOM (Vujinovi, *et al., 2019;* Shi & Schulin, 2019).

TOC indication of quantity, FDOM and CDOM

The TOC was connected to the quality of the DOM, where higher leaching of TOC often contains lower amounts of freshly, microbial produced DOM. This is in contrast to research in urban and waste water where fluorescence indices of labile OM have a strong positive correlation with TOC (Hudson *et al.,* 2008; Christian *et al.,* 2017). This shows that the amount of microbial matter was too low to impact the quality of DOM leached from the observation fields. The results instead shows that high presence of humic matter was the predominate form of TOC leached. All observation fields indicated a strong presence of humic matter and a small yet positive correlation with TOC. The reason behind this may be that humic matter that is more recalcitrant was to a higher extent accumulated in the soil and then transported by runoff. An increase of microbial produced OM that is more labile can increase the degradation of all types of SOM and enhance the soil CO_2 efflux (Garcia-Pausas & Paterson, 2011), which could reduce the amount of microbial matter leached form the soil. TOC was also connected to the MW of the OM, where higher TOC concentration indicates NOM with higher MW, while both E2:E3 and Slope showed significant reversed correlations. There was however no correlation between the S_{254}.

Alk, Cond and pH effects on FDOM and CODM

The Alk, Cond and pH all correlated strongly with each other. This was expected since the buffer capacity of the soil controls how sensitive the soil is to acidification. These parameters were also correlated with S_{254}, E2:E3 and Slope, where higher Alk, Cond and pH were linked to DOM with lower aromaticity and MW. Higher Alk, Cond and pH were also linked to more autochthonous and microbial produced DOM, as indicated by the significant correlation with BIX and C:T. These correlations are probably due to the sensitive nature of microorganisms. As was explained earlier, microbial organisms produce simpler OM and are very sensitive to changes in pH in the soil.

4.7. Measures against eutrophication and erosion

The last part of the discussion will be focusing on the linkage between water quality and leaching of POM and DOM. The biochemical oxygen demand (BOD) was not measured in this study. The correlation between fluorescence intensity for OM and BOD has however been established (Hur & Kong, 2007; Hudson *et al.,* 2008). The linkage between BOD and FDOM is stronger for the microbial and protein like indices than the humic indices, indicating that label NOM is easier utilised by microbes. This means that observation fields with higher FIX, BIX and lower C:T have higher amounts

of labile NOM and a higher risk for poor water quality. Hur & Kong (2007) investigated the effect of filtering and correlation between tryptophan, protein like fluorescent OM and BOD and found that filtering and the removal of SS had a negligible increase correlation to BOD. Therefore *UF* and *F45* samples and the comparison representing POM and DOM can be seen as predictors of BOD. TOC also has a strong correlation to BOD (Christian *et al.*, 2017) and should be accounted for when estimating the BOD of the observation fields. Hur & Kong (2007) and Hudson *et al.*, (2008) saw a positive correlation between TOC and FDOM, which was not observed in this study. Instead, a weak negative correlation between TOC, FIX_{F45} and BIX was observed and should therefore be considered when estimating the overall water quality. Without organic energy (TOC) degradation and cellular respiration of heterotrophs cannot take place, and the type of organic energy (FDOM) will therefore take a secondary role when determining water quality for observation fields. 21E had more microbial NOM but low TOC and could therefore be considered to have low to medium quality. 1D and 11M had high TOC and high intensity for $FIX_{UF,}$ BIX_{UF} and peak T_{UF}, indicating labile POM. The microbial NOM adsorbed onto the surface of SS is easily accessible for bacteria and can quickly be consumed (Postnikova, 2015). 1D and 11M also had large losses of tot-P linked to the TOC and losses of SS indicating erosion. 1D and 11M will therefore be considered to have low water quality with high eutrophication and erosion.

There are several steps that could be taken to better the eutrophication, erosion and quality conditions exhibited in soils 1D and 11M. First of all lime could be applied to 1D, as the low Ca^{2+} and pH are major causes of poor soil structure which leads to erosion and eutrophication (Singh *et al.*, 2016; Bronick & Lal 2005). Measures such as cover ditching and the establishment of protected zones to reduce surface runoff and leakage from the agricultural field if not already implemented is a good way to decrease leaching and erosion. Both 1D and 11M had cattle manure applied as fertilizer, and applying it under the right conditions is essential to minimize leaching of nutrients. Autumn had overall higher leaching of TOC, nutrients and more labile NOM connected to agricultural practices and a change towards a wetter weather and colder climate in NOV. The application of manure is therefore more sensitive during autumn and should be avoided if possible. Plants reduce water erosion by canopy cover and the rote zones stabilize the soil and increase aggregate formation. Therefore cover cropping is a good measurement to prevent leaching of P and erosion during autumn (Bronick & Lal 2005).

5. Conclusions

- Soil texture, weather and climate had significant effects on the source and origin of NOM. Loam soils with wet climate had higher leaching of terrestrial highly humified NOM, and loam and clay soils in dryer climate had higher leaching of more autochthonous microbial matter.

- Glacial clay soils 1D and 11M were determined to have high losses of adsorbed microbial matter to the surfaces of mineral particles as POM. This was probably caused by poorer soil structure and a steeper physical angle of slope which enhanced erosion of the soil. Loam soils 16Z and 21E had higher humification in the POM fraction probably caused by aggregation of smaller humic substances as an effect of high Ca^{2+} binding and acting like a glue between the negatively charged humic particles.

- Strong correlations between EEM indices were observed where origin and source were directly linked and terrestrial matter was correlated to humification. Correlations between absorbance indices were weaker but indicated a link between MW and aromaticity.

- EEM, Nutrient and abiotic correlations were harder to determine. Humification had a weak inverted link to loss of tot-P. FIX & BIX had an uncertain connection to tot-N and manure fertilization. Most observation fields with manure fertilization had a positive correlation between FIX & BIX and tot-N, which can be linked to an increase in mineralization and a higher activity of microorganisms.

- The seasonal pattern indicated a lower loading of autochthonous more microbial matter during winter and spring that gradually decreased until the month of November. In November the FIX & BIX indices increased sharply and then declined for POM while they increased steadily for DOM until December. The pattern observed during autumn was most likely caused by agricultural practices prior to the event as well as rewetting and heavy rain during the time period.

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Appendix

6.1. Appendix 1: Temporal differences.

The only significant seasonal difference for FIX was between the months of OCT_{UF} and JAN_{UF}. The *F45*, showed no significant seasonal variation (**Figure 5**). For BIX; OCT was significantly different from JAN, FEB, MAR, APR, and MAY with MAY_{UF} being significantly different from AUG_{UF} and DEC_{UF}. OCT_{F45} was significantly different from JAN_{F45}, MAR_{F45}, MAY_{F45} and JUN_{F45} (**Figure 5**). There are no significant differences regarding seasonal variation for HIX; *UF* and *F45*. There was a significant difference between MAY and OCT for C:T. OCT was significantly different from JUN and JUL, and JUN was significantly different from FEB; *F45* (**Figure 6**).

For $E2:E3_{UF}$, JAN and APR where significantly different from FEB and MAY. There was also a significant difference between NOV and JAN. For $E2:E3_{F45}$, JAN and APR are significantly different from FEB and JUL, MAY was significantly different from FEB, SEP was significantly different from APR and NOV was significantly different from FEB, JUL and SEP (**Figure 6**). Slope had no significant difference between months for the *F45*. NOV was significantly different from JAN, MAY, JUN. AUG and DEC (**Figure 6**).

For S_{254} *UF*, JAN was significantly different from OCT and DEC. For *F45*, FEB was significantly different from all other months except for JAN and NOV, and JAN was significantly different from MAR, APR, AUG, SEP and OCT (**Figure 7**).

A_{254} the spike for JAN_{UF} was significantly different from FEB_{UF}, MAR_{UF}, APR_{UF}, OCT_{UF}, NOV_{UF} and DEC_{UF}. With a trend towards lower A_{254} during late winter/early spring and autumn where FEB and MAR was significantly different from all other months except for OCT, NOV and DEC_{UF}. Late spring and summer months have an elevation in A_{254} where MAY and JUN was significantly different from FEB, MAR, OTC, NOV and DEC_{UF}. FEB and MAR where significantly different than JAN, APR, MAJ, JUN, JUL and $DECM_{F45}$. MAJ and JUN where significantly different from all other months except for JAN, JUL and DEC_{F45}. OCT and NOV where significantly different from JAN, MAJ, JUN and DEC: OCT was also significantly different from APR and JUL_{F45}. DEC was significantly different from JAN, MAJ and JUN_{F45} (**Figure 7**).

6.2. Appendix 2: Correlations for specific observation fields.

The top right corner are *F45* samples correlations and bottom left corner are *UF* samples correlations in the table. Values with (*) are significant (p<0, 05), (-) data not available.

1D	*Alk*	*Cond*	*pH*	*Tot N*	*NO2+3*	*Tot P*	*SS*	*TOC*	*FLOW*	*S_{254}*	*FIX*	*BIX*	*HIX*	*A_{254}*	*E2:E3*	*Slope*	*C:T*
Alk	#	0,19	-0,17	-0,16	-0,17	0,38	0,18	0,27	0,03	0,43	-0,33	-0,46	0,06	0,49*	-0,24	-0,34	-0,23
Cond	0	#	0,47	0,61*	0,69*	0,32	0,25	0,14	-0,12	-0,64	0,35	0,43	-0,11	-0,12	-0,63*	-0,28	-0,54*
pH	-0,31	0,54*	#	0,12	0,25	-0,29	-0,46	-0,26	-0,52*	-0,45	0,04	0,14	-0,05	-0,37	-0,35	0,36	-0,34
Tot N	-0,31	0,62*	0,27	#	0,98*	0,16	0,44*	-0,06	0,4	-0,7*	0,7*	0,82*	0	-0,41*	-0,19	-0,46*	-0,12
NO2+3	-0,44*	0,72*	0,49*	0,96*	#	0,06	0,37	-0,17	0,33	-0,69*	0,67*	0,84*	-0,05	-0,51*	-0,25	-0,37	-0,18
Tot P	0,46*	0,05	-0,42	0	-0,16	#	0,84*	0,75*	0,34	0,41	-0,02	-0,12	0,01	0,67*	-0,38	-0,56*	-0,11
SS	0,31	-0,04	-0,58*	0,22	0,06	0,87*	#	0,59*	0,58*	0,31	0,3	0,23	-0,11	0,39	-0,2	-0,63*	-0,05
TOC	0,42	-0,1	-0,45*	-0,22	-0,37*	0,77*	0,64*	#	0,16	0,14	-0,01	-0,25	0,21	0,78*	-0,26	-0,55*	0,02
FLOW	0,29	-0,26	-0,63*	0,15	-0,02	0,51*	0,69*	0,37	#	0,24	0,28	0,24	-0,18	0,11	0,09	-0,58*	0,13
S_{254}	0,2	-0,02	-0,66*	0,38*	0,28	0,5*	0,72*	0,18	0,58*	#	-0,5	-0,72*	-0,53	0,73*	-0,11	0,17	-0,33
FIX	0,02	0,01	-0,45*	0,43*	0,34	0,48*	0,74*	0,25	0,5*	0,82*	#	0,84*	-0,21	-0,38	0,12	-0,28	0,03
BIX	-0,16	0,1	-0,34	0,68*	0,61*	0,36	0,64*	0,06	0,47*	0,85*	0,85*	#	-0,31	-0,61*	0,08	-0,12	-0,13
HIX	-0,1	-0,26	0,34	-0,44*	-0,35	-0,67*	-0,78*	-0,39*	-0,46*	-0,82*	-0,79*	-0,8*	#	0,08	-0,27	-0,37	0,46*
A_{254}	0,49*	0,03	-0,53*	0,22	0,07	0,87*	0,83*	0,68*	0,51*	0,7*	0,64*	0,56*	-0,81*	#	-0,14	-0,27	-0,03
E2:E3	-0,19	-0,59*	-0,17	-0,44*	-0,45*	-0,36	-0,42*	-0,28	-0,14	-0,48*	-0,41*	-0,5*	0,6*	-0,5*	#	0,33	0,18
Slope	-0,16	-0,1	0,18	-0,32	-0,31	-0,14	-0,18	-0,22	-0,09	-0,33	-0,39*	-0,38*	0,4*	-0,51*	0,39*	#	-0,15
C:T	-0,12	-0,29	0,24	-0,42*	-0,39*	-0,54*	-0,65*	-0,26	-0,31	-0,81*	-0,71*	-0,8*	0,91*	-0,73*	0,68*	0,44*	#

20E	*Alk*	*Cond*	*pH*	*Tot N*	*NO2+NO3*	*Tot P*	*SS*	*TOC*	*FLOW*	*S_{254}*	*FIX*	*BIX*	*HIX*	*A_{254}*	*E2:E3*	*Slope*	*C:T*
Alk	#	0,97*	0,24	-0,9*	-0,96*	-0,57*	-0,85*	-0,74*	0,28	0,64*	0,9*	0,91*	-0,82*	-0,88*	0,49	0,55*	-0,91*
Cond	0,97*	#	0,16	-0,87*	-0,9*	-0,58*	-0,85*	-0,76*	0,33	0,64*	0,89*	0,94*	-0,85*	-0,86*	0,49	0,6*	-0,91*
pH	0,42	0,38	#	-0,59*	-0,52	-0,56*	-0,28	-0,39	-0,33	-0,08	-0,03	0,04	0,04	-0,24	0,13	-0,1	0,09
Tot N	-0,9*	-0,84*	-0,58*	#	0,94*	0,54*	0,84*	0,61*	0,23	-0,1	-0,6*	-0,49*	0,52*	0,37	-0,5*	-0,44*	0,62*
NO2+NO3	-0,93*	-0,86*	-0,54*	0,96*	#	0,39	0,76*	0,45*	0,24	-0,24	-0,54*	-0,43*	0,47*	0,31	-0,46*	-0,49*	0,65*
Tot P	-0,54*	-0,46	-0,62*	0,64*	0,51*	#	0,68*	0,87*	-0,18	0,17	-0,56*	-0,67*	0,6*	0,45*	-0,33	0,06	0,62*
SS	-0,59*	-0,43	-0,13	0,83*	0,75*	0,74*	#	0,8*	0,08	-0,1	-0,68*	-0,52*	0,51*	0,27	-0,4	-0,37	0,63*
TOC	-0,72*	-0,66*	-0,5	0,7*	0,57*	0,9*	0,82*	#	-0,1	0,21	-0,63*	-0,74*	0,69*	0,44*	-0,42	-0,08	0,65*
FLOW	0,22	0,31	-0,03	0,29	0,29	0	0,41*	0,05	#	0,08	0,13	0,25	-0,2	-0,46*	0,31	0,3	-0,04
S_{254}	-0,6*	-0,58*	-0,49	0,16	0,28	-0,05	-0,11	-0,09	-0,4*	#	-0,27	-0,43*	0,36	0,39	0,08	0,53*	0,07
FIX	0,73*	0,75*	0,23	-0,53*	-0,54*	-0,38	-0,42*	-0,52*	0,1	-0,31	#	0,79*	-0,75*	-0,61*	0,2	0,2	-0,75*
BIX	0,88*	0,85*	0,31	-0,64*	-0,61*	-0,63*	-0,58*	-0,71*	0,05	-0,23	0,8*	#	-0,92*	-0,65*	0,29	-0,04	-0,84*
HIX	0,3	0,23	0,43	-0,13	-0,1	-0,28	-0,22	-0,16	0,08	-0,04	-0,14	-0,25	#	0,61*	-0,19	-0,03	0,84*
A_{254}	-0,8*	-0,76*	-0,5*	0,56*	0,47*	0,71*	0,58*	0,67*	-0,2	0,43*	-0,59*	-0,71*	-0,2	#	-0,49*	-0,28	0,43*
E2:E3	0,66*	0,62*	0,47	-0,35	-0,33	-0,5*	-0,17	-0,33	0,45*	-0,47*	0,37*	0,29	0,5*	-0,62*	#	0,55*	-0,13
Slope	0,75*	0,73*	0,51*	-0,4*	-0,4*	-0,27	-0,09	-0,13	0,35	-0,65*	0,1	0,16	0,24	-0,47*	0,61*	#	-0,06
C:T	-0,47	-0,5*	-0,08	0,41*	0,49*	0,14	0,2	0,25	0,19	0,01	-0,5*	-0,63*	0,57*	0,11	0,09	-0,07	#

21E	Alk	Cond	pH	Tot N	NO2+NO3	Tot P	SS	TOC	FLOW	S_{254}	FIX	BIX	HIX	A_{254}	E2:E3	Slope	C:T
Alk	#	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cond	-	#	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
pH	-	-	#	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Tot N	-	-	-	#	0,9*	-0,01	0,18	0,04	0,28	0,66*	-0,4	-0,35	0,65*	0,69*	-0,69*	-0,13	0,43
NO2+NO3	-	-	-	0,92*	#	-0,11	0,14	-0,13	0,3	0,69*	-0,51	-0,32	0,62*	0,69*	-0,53	0,05	0,35
Tot P	-	-	-	0,11	0,04	#	0,5	0,29	-0,47	0,15	0,07	-0,65*	0,33	-0,24	-0,08	0,14	0,36
SS	-	-	-	0,2	0,18	0,54*	#	0,54	-0,56*	0,41	-0,42	-0,37	0,01	0,23	-0,27	0,1	-0,13
TOC	-	-	-	0,06	-0,08	0,34	0,53*	#	-0,05	0,3	-0,37	-0,29	-0,23	0,19	-0,04	-0,03	0,12
FLOW	-	-	-	0,42	0,44	-0,32	-0,44	-0,01	#	0,05	-0,42	-0,07	0,12	0,45	-0,17	0,12	0,27
S_{254}	-	-	-	0,56*	0,73*	-0,22	-0,04	-0,34	0,35	#	-0,47	-0,52	0,46	0,72*	-0,52	0,12	0,15
FIX	-	-	-	0,58*	0,54*	-0,44	-0,28	-0,25	0,56*	0,34	#	0,08	0,09	-0,56*	0,18	-0,07	0,2
BIX	-	-	-	-0,22	-0,25	-0,85*	-0,48	-0,4	0,02	0	0,29	#	-0,66*	-0,28	0,57*	-0,46	-0,61*
HIX	-	-	-	0,05	0,04	0,46	-0,06	0,2	0,34	-0,12	-0,16	-0,61*	#	0,2	-0,59*	0,31	0,76*
A_{254}	-	-	-	0,61*	0,72*	-0,03	0,14	-0,03	0,24	0,89*	0,01	-0,1	0,07	#	-0,61*	-0,12	-0,09
E2:E3	-	-	-	-0,14	-0,16	0,5	0,34	0,29	-0,08	-0,45	-0,17	-0,44	0,15	-0,51	#	-0,06	-0,35
Slope	-	-	-	-0,13	0,06	0,35	0,47	0,11	-0,34	0,31	-0,4	-0,42	0,18	0,25	-0,01	#	0,33
C:T	-	-	-	0,05	-0,01	0,46	-0,09	0,37	0,38	-0,24	-0,15	-0,64*	0,9*	-0,08	0,17	0,06	#

6E	Alk	Cond	pH	Tot N	NO2+NO3	Tot P	SS	TOC	FLOW	S_{254}	FIX	BIX	HIX	A_{254}	E2:E3	Slope	C:T
Alk	#	0,72*	-0,19	-	-	-	-	0,25	-0,29	-0,07	-0,04	-0,31	0	0,29	-0,13	-0,21	-0,13
Cond	0,4*	#	-0,53*	-	-	-	-	0,19	0,29	0	0,28	-0,01	-0,02	0,34*	-0,06	-0,4*	-0,06
pH	0,01	-0,66*	#	-	-	-	-	-0,05	-0,24	-0,17	-0,36*	-0,27	0,29	-0,13	0,34*	0,21	0,29
Tot N	-0,32	-0,03	0,46	#	0,97*	0,16	0,05	0,78*	0,68*	-0,2	0,16	-0,12	0,06	0,13	0,35	0,44	0,44
NO2+NO3	-0,6	-0,03	0,49	0,98*	#	0,14	0,07	0,7*	0,7*	-0,27	0,08	-0,09	0,01	0,18	0,31	0,39	0,41
Tot P	0,09	-0,2	0,49	0,4	0,36	#	0,29	0,21	0,16	0,1	-0,41	-0,35	0,48	0,57*	-0,05	-0,2	0,25
SS	-0,54	0,31	0,09	0,39	0,39	0,33	#	-0,14	0,19	0,28	0,22	0,03	0,25	0,48	0,15	0,09	0,14
TOC	0,13	0,3	-0,2	0,87*	0,81*	0,48*	0,32	#	0,18	-0,42*	-0,09	-0,16	0,11	-0,09	-0,05	-0,12	0,09
FLOW	-0,26	0,6	-1*	0,64*	0,66*	0,54*	0,4	0,7*	#	-0,57*	0,43*	0,41*	-0,17	-0,35*	0,13	-0,38*	0,03
S_{254}	-0,17	-0,19	-0,01	-0,31	-0,3	-0,09	0,27	-0,64*	-0,19	#	-0,24	-0,25	0,32*	0,6*	-0,12	0,34*	0,26
FIX	-0,19	0,45*	-0,57*	0,22	0,28	-0,16	0,2	0,07	-0,13	-0,23	#	0,74*	-0,43*	-0,35*	-0,05	-0,43*	-0,33*
BIX	-0,28	0,17	-0,35*	-0,57*	-0,49*	-0,55*	-0,12	-0,08	-0,47	-0,37*	0,65*	#	-0,57*	-0,58*	-0,14	-0,39*	-0,52*
HIX	0,02	-0,13	0,26	0,3	0,32	0,23	-0,01	0,13	0,25	-0,06	-0,27	-0,56*	#	0,35*	0,15	-0,03	0,77*
A_{254}	-0,12	0,34*	-0,3	0,34	0,3	0,27	0,48*	0,01	0,31	0,68*	-0,19	-0,53*	0,18	#	-0,14	0,2	0,31*
E2:E3	-0,12	-0,02	0,23	0,37	0,36	0,29	0,05	0,23	0,09	-0,42*	0,03	-0,08	0,31*	-0,13	#	0,31*	0,04
Slope	-0,26	-0,46*	0,32*	0,56*	0,55*	0,43	0,11	-0,19	0,17	0,39*	-0,37*	-0,52*	0,3*	0,46*	0,15	#	-0,07
C:T	-0,2	0,09	0,11	0,65*	0,62*	0,32	0,28	0,34*	0,53*	0,08	-0,31*	-0,66*	0,71*	0,44*	0,13	0,31*	#

7E	Alk	Cond	pH	Tot N	NO2+NO3	Tot P	SS	TOC	FLOW	S_{254}	FIX	BIX	HIX	A_{254}	E2:E3	Slope	C:T
Alk	#	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cond	-	#	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
pH	-	-	#	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Tot N	-	-	-	#	0,98*	0,66*	0,87*	0,88*	0,38	0,12	-0,63*	-0,34	0,43	0,33	0,03	-0,08	0,44
NO2+NO3	-	-	-	0,96*	#	0,56*	0,84*	0,8*	0,44	0,16	-0,61*	-0,3	0,41	0,28	0,08	-0,02	0,43
Tot P	-	-	-	0,77*	0,67*	#	0,8*	0,84*	0,04	-0,31	-0,34	-0,33	0,28	0,44	0,05	-0,24	0,34
SS	-	-	-	0,88*	0,82*	0,83*	#	0,91*	0,39	-0,04	-0,46	-0,24	0,46	0,31	0,19	-0,07	0,55*
TOC	-	-	-	0,91*	0,83*	0,91*	0,91*	#	0,29	-0,14	-0,58*	-0,38	0,49	0,35	0,09	-0,22	0,47
FLOW	-	-	-	0,41	0,51	-0,06	0,34	0,24	#	0,09	0,05	0,32	-0,1	-0,22	-0,16	0,1	-0,21
S_{254}	-	-	-	-0,4	-0,41	-0,36	-0,63*	-0,47*	-0,35	#	-0,45	-0,32	0,42	0,65*	-0,03	-0,03	0,27
FIX	-	-	-	-0,28	-0,32	-0,2	-0,25	-0,21	-0,06	0,17	#	0,54*	-0,56*	-0,66*	-0,18	-0,01	-0,38
BIX	-	-	-	-0,48*	-0,55*	-0,31	-0,46*	-0,51*	-0,17	0,62*	0,32	#	-0,88*	-0,35	-0,17	0,15	-0,6*
HIX	-	-	-	0	0,06	-0,12	0,12	0,06	0,32	-0,63*	0,37	-0,58*	#	0,34	0,25	-0,16	0,81*
A_{254}	-	-	-	0,7*	0,64*	0,68*	0,51*	0,71*	0,15	0,2	-0,22	-0,3	-0,29	#	0,07	-0,28	0,35
E2:E3	-	-	-	-0,13	-0,02	-0,31	-0,13	-0,2	-0,03	-0,27	-0,17	-0,14	0,27	-0,45*	#	0,42	0,43
Slope	-	-	-	-0,08	0	-0,1	0,09	-0,13	-0,11	-0,38	-0,23	0,04	-0,05	-0,42	0,53*	#	-0,1
C:T	-	-	-	0,41	0,46*	0,28	0,47*	0,44	0,28	-0,69*	0,01	-0,84*	0,74*	0,12	0,2	0,05	#

11M	Alk	Cond	pH	Tot N	NO2+NO3	Tot P	SS	TOC	FLOW	S_{254}	FIX	BIX	HIX	A_{254}	E2:E3	Slope	C:T
Alk	#	0,3	0,76*	-0,33	-0,29	-0,45*	-0,25	-0,45*	0,16	0,12	0,13	-0,07	0,3	-0,48*	0,28	0,62*	0,05
Cond	0,28	#	0,47*	0,54*	0,53*	-0,52*	-0,2	-0,39	-0,09	-0,27	0,7*	0,82*	-0,1	-0,7*	0,7*	0,05	-0,07
pH	0,76*	0,45*	#	-0,05	0,08	-0,44*	0,05	-0,3	0,06	0,17	0,3	0,22	0,03	-0,61*	0,37	0,41	0,13
Tot N	-0,3	0,59*	0,02	#	0,97*	-0,06	-0,12	0,14	-0,26	0,28	0,52*	0,63*	-0,05	-0,04	0,41*	0,08	0,08
NO2+NO3	-0,26	0,59*	0,12	0,84*	#	-0,21	-0,25	-0,02	-0,37*	0,22	0,45*	0,56*	-0,1	-0,06	0,4*	0,06	0
Tot P	-0,42	-0,52*	-0,42	-0,22	-0,51*	#	0,82*	0,79*	0,31	0,2	-0,27	-0,21	-0,07	0,37*	-0,14	-0,15	0,07
SS	-0,17	-0,23	0,16	-0,3	-0,59*	0,9*	#	0,72*	0,63*	0,18	-0,29	-0,13	0,12	0,08	-0,03	0,02	0,36
TOC	-0,44	-0,42	-0,25	0,04	-0,3	0,77*	0,73*	#	0,29	0,23	-0,14	0,03	-0,03	0,36*	-0,06	-0,16	0,15
FLOW	0,18	-0,1	0,09	-0,27	-0,52*	0,48*	0,66*	0,45*	#	0,07	-0,25	-0,07	-0,01	-0,15	0,06	0,09	0,29
S_{254}	-0,37	-0,57*	-0,46*	-0,22	-0,25	0,14	0,11	0,12	0,3	#	0,06	0,07	0,4*	0,15	0,24	0,36*	0,32
FIX	-0,13	0,36	0,09	0,49*	0,28	0,16	0,09	0,46*	0,25	-0,02	#	0,86*	-0,02	-0,6*	0,38*	0,32	-0,05
BIX	-0,22	0,26	0,17	0,35*	0,34*	0	0,07	0,32*	0,18	0,24	0,6*	#	-0,11	-0,61*	0,47*	0,23	0,01
HIX	0,44*	0,49*	0,29	0,06	0,17	-0,34*	-0,34*	-0,53*	-0,41*	-0,74*	-0,23	-0,53*	#	0,04	0,13	0,32	0,54*
A_{254}	-0,49*	-0,69*	-0,43	-0,18	-0,39*	0,54*	0,51*	0,67*	0,37*	0,77*	0,13	0,31*	-0,86*	#	-0,38*	-0,36*	-0,07
E2:E3	0,5*	0,57*	0,42	0,23	0,3	-0,25	-0,2	-0,43*	-0,21	-0,77*	-0,03	-0,33*	0,77*	-0,8*	#	0,23	0,2
Slope	0,67*	0,09	0,45*	0,03	0,18	-0,35*	-0,27	-0,46*	-0,2	-0,42*	-0,32*	-0,32*	0,61*	-0,55*	0,51*	#	0,16
C:T	0,3	0,38	0,25	-0,03	-0,05	-0,11	-0,01	-0,29	-0,12	-0,68*	-0,21	-0,57*	0,87*	-0,65*	0,71*	0,5*	#

2M	Alk	Cond	pH	Tot N	NO2+NO3	Tot P	SS	TOC	FLOW	S_{254}	FIX	BIX	HIX	A_{254}	E2:E3	Slope	C:T
Alk	#	0,93*	0,54*	-0,72*	-0,72*	-0,31	0,08	0,23	-0,47*	-0,36*	0,11	-0,38*	0,29	0,41*	-0,51*	-0,23	0,13
Cond	0,92*	#	0,52*	-0,66*	-0,66*	-0,36*	0,16	0,23	-0,43*	-0,44*	0,03	-0,38*	0,33*	0,33*	-0,55*	-0,2	0,19
pH	0,49*	0,52*	#	-0,67*	-0,72*	-0,69*	0,01	-0,27	-0,75*	-0,42*	0,26	-0,08	-0,06	0,14	-0,39*	0,1	-0,1
Tot N	-0,69*	-0,61*	-0,67*	#	0,98*	0,31*	-0,1	0,18	0,55*	0,43*	-0,33*	0,04	0,08	-0,09	0,45*	0,16	0,06
NO2+NO3	-0,7*	-0,63*	-0,74*	0,98*	#	0,29	-0,09	0,15	0,54*	0,44*	-0,38*	0	0,14	-0,08	0,46*	0,21	0,09
Tot P	-0,31	-0,45*	-0,77*	0,43*	0,33*	#	0,31*	0,39*	0,51*	0,31*	-0,02	0,13	-0,07	-0,13	0,31*	0,04	0,04
SS	0,07	0,2	0,2	-0,14	-0,04	0,01	#	0,34*	-0,04	-0,15	-0,22	-0,22	0,34*	-0,03	-0,27	-0,17	0,1
TOC	0,18	0,15	-0,36*	0,27	0,19	0,46*	0,22	#	0,15	0,11	-0,4*	-0,55*	0,34*	0,67*	-0,18	-0,19	0,44*
FLOW	-0,47*	-0,48*	-0,81*	0,57*	0,53*	0,59*	-0,18	0,21	#	-0,01	-0,4*	-0,02	0,04	-0,12	0,18	-0,16	0,28*
S_{254}	0,01	-0,04	0,23	-0,27	-0,24	-0,38*	-0,34*	-0,33*	-0,09	#	0,23	0,33*	-0,16	-0,17	0,32*	0,57*	-0,23
FIX	-0,05	-0,16	0,04	-0,14	-0,22	0,11	-0,42*	-0,34*	-0,19	0,2	#	0,65*	-0,56*	-0,46*	0,09	0,27	-0,62*
BIX	-0,24	-0,29	0,04	-0,12	-0,18	0,01	-0,29*	-0,49*	-0,1	0,22	0,73*	#	-0,7*	-0,71*	0,42*	0,36*	-0,71*
HIX	0,16	0,25	0,09	0,05	0,21	-0,21	0,28*	0,05	-0,02	-0,2	-0,58*	-0,76*	#	0,34*	-0,21	-0,37*	0,69*
A_{254}	0,17	0,1	-0,28	0,1	0,07	0,23	-0,03	0,72*	0,23	0,33*	-0,26	-0,43*	0,02	#	-0,28*	-0,28	0,41*
E2:E3	0,01	0,03	-0,03	0,18	0,12	0,14	-0,16	-0,11	0,01	-0,41*	0,04	0,13	-0,05	-0,4*	#	0,34*	-0,15
Slope	-0,11	0	0,23	0,18	0,19	0,04	-0,09	-0,05	-0,3*	-0,17	0,23	0,22	-0,24	-0,22	0,32*	#	-0,3*
C:T	-0,05	-0,07	-0,18	0,2	0,17	0,03	0	0,36*	0,34*	-0,01	-0,56*	-0,62*	0,53*	0,36*	-0,17	-0,35*	#

12N	Alk	Cond	pH	Tot N	NO2+NO3	Tot P	SS	TOC	FLOW	S_{254}	FIX	BIX	HIX	A_{254}	E2:E3	Slope	C:T
Alk	#	-0,47*	-0,13	-0,76*	-0,73*	0,62*	0,48*	0,69*	-0,18	-0,2	-0,28	-0,45*	-0,09	0,83*	-0,15	-0,1	-0,17
Cond	-0,42*	#	-0,46*	0,86*	0,87*	-0,25	-0,19	-0,42*	0,47*	0,55*	0,45*	0,79*	-0,01	-0,44*	0,34	0,25	-0,03
pH	-0,31	-0,43*	#	-0,27	-0,23	-0,15	-0,18	-0,09	-0,65*	-0,14	-0,02	-0,18	-0,19	-0,2	-0,31	-0,19	0,03
Tot N	-0,74*	0,85*	-0,15	#	0,99*	-0,5*	-0,26	-0,56*	0,39*	0,51*	0,47*	0,62*	-0,06	-0,51*	0,33*	0,24	0,01
NO2+NO3	-0,72*	0,85*	-0,11	0,99*	#	-0,5*	-0,24	-0,58*	0,38*	0,53*	0,48*	0,63*	-0,09	-0,48*	0,33*	0,29	0,02
Tot P	0,49*	-0,2	-0,23	-0,41*	-0,42*	#	0,37*	0,48*	-0,23	0,01	-0,22	-0,42*	0,14	0,55*	-0,31*	-0,24	-0,32*
SS	0,25	-0,09	-0,22	-0,11	-0,11	0,36*	#	0,45*	0,16	-0,06	0,08	-0,04	-0,06	0,37*	0,11	0,2	-0,19
TOC	0,74*	-0,3	-0,35*	-0,48*	-0,51*	0,45*	0,32*	#	0,22	-0,48*	-0,29	-0,3*	-0,05	0,62*	-0,15	-0,14	-0,03
FLOW	0,15	0,4*	-0,68*	0,3*	0,27	-0,16	0,1	0,41*	#	-0,13	0,06	0,25	-0,07	0,04	0,28	0,24	0,25
S_{254}	0,31	-0,14	-0,14	-0,16	-0,16	0,04	-0,02	-0,08	0,11	#	0,07	0,15	0,25	-0,11	0,2	0,17	-0,11
FIX	-0,11	0,63*	-0,38*	0,58*	0,58*	-0,13	0,1	-0,09	0,25	-0,06	#	0,6*	-0,34*	-0,39*	0,28	0,47*	-0,18
BIX	-0,6*	0,82*	-0,15	0,62*	0,64*	-0,19	-0,01	-0,49*	0,05	-0,15	0,49*	#	-0,33*	-0,41*	0,26	0,21	-0,16
HIX	-0,31	0,24	-0,05	0,37*	0,34*	-0,33*	-0,01	-0,18	0,25	0,04	0,2	0,01	#	0,02	-0,15	-0,01	0,26
A_{254}	0,85*	-0,35*	-0,45*	-0,47*	-0,5*	0,48*	0,26	0,79*	0,34*	0,41*	-0,16	-0,55*	-0,08	#	-0,25	-0,08	-0,1
E2:E3	0,09	0,17	-0,08	0,08	0,05	-0,12	-0,08	0,17	0,13	-0,33*	0,12	0,14	0,15	-0,04	#	0,5*	0,14
Slope	0,03	0,15	-0,19	0,22	0,18	-0,09	0,06	0,02	0,24	0,13	0,26	0	0,07	0,01	0,25	#	0,16
C:T	0,21	-0,02	-0,11	-0,04	-0,04	-0,38*	0,06	0,21	0,5*	0,11	0,04	-0,2	0,45*	0,11	0,29*	0,19	#

4O	Alk	Cond	pH	Tot N	NO2+NO3	Tot P	SS	TOC	FLOW	S_{254}	FIX	BIX	HIX	A_{254}	E2:E3	Slope	C:T
Alk	#	0,39	0,42	-0,61*	-0,51*	-0,43	-0,52*	-0,7*	-0,76*	0,66*	0,11	0,47*	0,45	-0,58*	0,1	0,45	-0,22
Cond	0,31	#	0,19	0,14	0,27	0,26	0,11	0,03	-0,48	0,07	0,43	0,49*	0,02	0,21	-0,02	-0,15	-0,27
pH	0,41	0,26	#	0,01	-0,09	-0,35	-0,29	-0,36	-0,43	0,34	0,44	0,41	0,09	-0,64*	0,36	0,35	0,1
Tot N	-0,7*	0,17	0,03	#	0,99*	-0,4*	-0,26	0,04	0,03	0,22	-0,05	-0,12	0,23	0,54*	0,27	0,18	0,2
NO2+NO3	-0,56*	0,28	-0,05	0,99*	#	-0,42*	-0,29	0,03	-0,02	0,19	-0,01	-0,16	0,31	0,61*	0,18	0,1	0,17
Tot P	-0,43	-0,13	-0,53*	-0,44*	-0,49*	#	0,95*	0,53*	0,07	-0,55*	0,12	0,03	-0,41*	-0,17	-0,02	-0,32	-0,11
SS	-0,46*	-0,25	-0,47*	-0,29	-0,34	0,94*	#	0,55*	0,1	-0,58*	0,16	0,06	-0,35	-0,1	0,07	-0,31	-0,06
TOC	-0,63*	-0,31	-0,5*	0,01	-0,03	0,54*	0,57*	#	0,66*	-0,2	-0,27	-0,56*	-0,04	0,46*	-0,05	-0,25	0,46*
FLOW	-0,63*	-0,47*	-0,56*	0,19	0,09	0,1	0,16	0,67*	#	-0,23	-0,28	-0,41*	-0,03	0,41*	-0,15	-0,15	0,56*
S_{254}	-0,17	-0,12	-0,58*	0,11	0,12	-0,2	-0,16	0,11	0,54*	#	-0,22	0,05	0,31	0,11	0,07	0,48*	-0,06
FIX	0,14	0,23	0,4	0,05	0,07	0,05	0,13	-0,11	-0,1	-0,27	#	0,58*	-0,01	-0,38*	0,06	-0,05	-0,2
BIX	0,09	0,31	0,12	-0,38*	-0,38*	0,25	0,24	-0,03	-0,03	0,07	0,42*	#	-0,21	-0,47*	0,03	0,07	-0,55*
HIX	0,57*	0,22	0,64*	0,21	0,18	-0,45*	-0,41*	-0,52*	-0,5*	-0,52*	0,05	-0,46*	#	0,08	0,03	0,18	0,34
A_{254}	-0,56*	-0,23	-0,72*	0,07	0,11	0,24	0,28	0,77*	0,75*	0,68*	-0,24	0,03	-0,72*	#	-0,25	-0,19	0,25
E2:E3	0,59*	0,25	0,51*	0,18	0,24	-0,26	-0,24	-0,57*	-0,54*	-0,44*	0,19	-0,19	0,64*	-0,62*	#	0,19	0,26
Slope	0,59*	0,16	0,61*	0,01	-0,04	-0,46*	-0,4*	-0,55*	-0,45*	-0,45*	0,09	-0,19	0,86*	-0,72*	0,54*	#	0,07
C:T	0,01	-0,34	0,34	0,32	0,27	-0,27	-0,18	-0,01	0,07	-0,4*	-0,04	-0,55*	0,7*	-0,27	0,36*	0,58*	#

5O	Alk	Cond	pH	Tot N	NO2+NO3	Tot P	SS	TOC	FLOW	S_{254}	FIX	BIX	HIX	A_{254}	E2:E3	Slope	C:T
Alk	#	0,76*	0,2	-0,53*	-0,46*	-0,42*	-0,54*	-0,65*	-0,22	0,22	0,28	0,12	-0,06	-0,35	-0,1	0,49*	-0,44*
Cond	0,79*	#	0	-0,18	-0,14	-0,36	-0,31	-0,53*	-0,08	0,33	0,28	0,16	0	-0,27	-0,16	0,47*	-0,49*
pH	0,23	0,23	#	0,19	0,25	-0,49*	-0,47*	-0,39*	0,35	0,08	0,07	0,28	-0,08	-0,48*	0,13	0,06	0,06
Tot N	-0,52*	-0,16	0,27	#	0,99*	-0,21	0,28	0,13	0,21	0,4*	0,08	0,06	0,14	0,14	-0,05	-0,14	0,33*
NO2+NO3	-0,35*	-0,02	0,36*	0,98*	#	-0,27	0,2	0,07	0,22	0,41*	0,13	0,1	0,1	0,09	-0,03	-0,11	0,29
Tot P	-0,49*	-0,5*	-0,6*	-0,15	-0,24	#	0,69*	0,81*	-0,27	-0,44*	-0,44*	-0,55*	0,27	0,54*	-0,16	-0,45*	0,35*
SS	-0,52*	-0,44*	-0,59*	0,26	0,15	0,75*	#	0,7*	-0,01	-0,03	-0,32*	-0,35*	0,22	0,46*	-0,11	-0,37*	0,39*
TOC	-0,65*	-0,6*	-0,51*	0,14	0,05	0,84*	0,75*	#	-0,18	-0,23	-0,45*	-0,55*	0,31*	0,61*	-0,21	-0,47*	0,54*
FLOW	-0,12	-0,06	0,08	0,21	0,18	-0,13	0,14	-0,05	#	-0,11	-0,09	0,28	-0,33*	-0,43*	0,11	0,03	0,04
S_{254}	-0,11	-0,25	-0,32	-0,08	-0,06	0,07	0,05	-0,09	-0,5*	#	0,29	0,14	0,19	0,07	0,11	0,38*	0,09
FIX	0,06	0,16	0,06	0,13	0,16	-0,24	-0,24	-0,32*	-0,29*	0,15	#	0,53*	-0,45*	-0,46*	0,31*	0,61*	-0,55*
BIX	0,03	0,11	0,33	0,15	0,2	-0,43*	-0,23	-0,45*	0,08	0,08	0,53*	#	-0,71*	-0,75*	0,54*	0,57*	-0,64*
HIX	0,25	0,2	0,19	0,09	0,09	-0,31*	-0,08	-0,18	0,17	-0,23	-0,28*	-0,37*	#	0,63*	-0,37*	-0,49*	0,6*
A_{254}	-0,52*	-0,54*	-0,64*	0,04	-0,03	0,75*	0,62*	0,71*	-0,29*	0,51*	-0,24	-0,46*	-0,28*	#	-0,43*	-0,44*	0,5*
E2:E3	0,52*	0,42*	0,54*	-0,06	0	-0,54*	-0,44*	-0,43*	0,26	-0,34*	-0,06	0,21	0,29*	-0,63*	#	0,42*	-0,37*
Slope	0,49*	0,46*	0,26	-0,03	0,03	-0,55*	-0,38*	-0,51*	-0,04	-0,16	0,17	0,23	0,46*	-0,6*	0,64*	#	-0,51*
C:T	-0,17	-0,25	-0,06	0,17	0,13	0,03	0,05	0,25	0,28	-0,3*	-0,48*	-0,63*	0,63*	0,03	0,03	0	#

16Z	*Alk*	*Cond*	*pH*	*Tot N*	*NO2+NO3*	*Tot P*	*SS*	*TOC*	*FLOW*	*S_{254}*	*FIX*	*BIX*	*HIX*	*A_{254}*	*E2:E3*	*Slope*	*C:T*
Alk	#	0,86*	0,3	-0,62*	-0,64*	-0,68*	0,25	-0,39*	-0,56*	-0,16	0,23	-0,18	0,36	0,1	-0,18	-0,04	0,11
Cond	0,88*	#	0,06	-0,51*	-0,53*	-0,61*	0,3	-0,5*	-0,46*	0,05	-0,04	-0,27	0,52*	0,17	-0,25	0,04	0,17
pH	0,23	0,03	#	-0,15	-0,1	-0,08	-0,13	-0,48*	-0,62*	-0,43*	0,58*	0,35	-0,23	-0,45*	-0,35	-0,04	-0,12
Tot N	-0,64*	-0,56*	-0,11	#	0,97*	0,4*	-0,11	0	0,45*	-0,37*	0,33*	0,46*	-0,41*	-0,6*	0,18	-0,35*	-0,18
NO2+NO3	-0,66*	-0,59*	-0,06	0,97*	#	0,41*	-0,07	0	0,49*	-0,31	0,35*	0,5*	-0,38*	-0,6*	0,24	-0,28	-0,17
Tot P	-0,47*	-0,39*	0,01	0,41*	0,39*	#	-0,05	0,03	0,25	0,15	-0,17	-0,17	-0,22	-0,02	-0,07	-0,12	0,04
SS	0,17	0,22	-0,15	-0,11	-0,07	0	#	-0,06	-0,04	-0,04	-0,14	-0,1	0,19	0,19	0,05	-0,11	0,1
TOC	-0,22	-0,32	-0,48*	-0,05	-0,05	-0,05	0,02	#	0,45*	0,09	-0,16	-0,09	-0,24	0,3	0,15	-0,1	-0,21
FLOW	-0,59*	-0,52*	-0,58*	0,45*	0,5*	0,19	-0,04	0,42*	#	-0,05	0,03	0,17	-0,11	0,04	0,4*	-0,09	-0,22
S_{254}	0,44*	0,48*	0,21	-0,39*	-0,35*	-0,08	0,16	-0,42*	-0,13	#	-0,36*	-0,35*	0,29	0,49*	-0,17	0,49*	0,19
FIX	0,38*	0,18	0,45*	0,2	0,21	-0,37*	-0,12	-0,22	-0,02	-0,2	#	0,67*	-0,33*	-0,58*	0,15	-0,11	-0,15
BIX	-0,26	-0,32	0,3	0,59*	0,64*	0,02	-0,18	-0,13	0,19	-0,47*	0,62*	#	-0,38*	-0,61*	0,14	-0,03	-0,32*
HIX	0,25	0,25	-0,21	-0,38*	-0,39*	-0,49*	0,15	-0,1	-0,09	0,16	0,07	-0,23	#	0,07	-0,03	0,15	0,65*
A_{254}	0,08	0,05	-0,42*	-0,39*	-0,36*	-0,11	0,12	0,27	0,28	0,69*	-0,36*	-0,62*	0,05	#	-0,24	0,03	-0,1
E2:E3	0,14	-0,01	-0,17	-0,01	-0,01	-0,09	-0,01	0,13	-0,03	-0,44*	0,11	0,15	0,19	-0,29	#	0,16	0,09
Slope	0,05	0,17	-0,05	-0,48*	-0,43*	-0,15	0,04	0,03	-0,14	0,18	-0,3*	-0,24	0,27	0,08	0,19	#	0,17
C:T	0,3	0,13	0,07	-0,35*	-0,35*	-0,39*	0,01	-0,05	-0,1	0,02	0,22	-0,12	0,69*	0	0,28	0,14	#

14AC	*Alk*	*Cond*	*pH*	*Tot N*	*NO2+NO3*	*Tot P*	*SS*	*TOC*	*FLOW*	*S_{254}*	*FIX*	*BIX*	*HIX*	*A_{254}*	*E2:E3*	*Slope*	*C:T*
Alk	#	-0,64	0,99*	-0,3	-0,28	0,3	-0,36	0,22	-0,52	-	0,08	0,05	0,05	-0,07	-0,15	0,27	-0,32
Cond	-0,63	#	-0,77*	-0,33	-0,32	-0,79*	-0,54	-0,66*	0,56	-	-0,15	-0,06	-0,04	-0,11	-0,11	0,17	0,09
pH	0,99*	-0,79*	#	-0,05	-0,05	0,52	0,09	0,43	-0,67*	-	0,27	0,21	0,15	0,26	-0,13	-0,1	-0,07
Tot N	-0,45	-0,37	0,02	#	0,99*	0,11	0,53	0,74*	-0,25	-	0,49	0,08	0,25	0,07	-0,02	-0,44	0,34
NO2+NO3	-0,42	-0,33	-0,08	0,98*	#	0,13	0,57	0,76*	-0,2	-	0,56*	0,16	0,27	0,09	-0,08	-0,42	0,35
Tot P	0,1	-0,67*	0,43	0,08	0,02	#	0,69*	0,54	-0,32	-	0,29	0,31	-0,24	0,2	-0,3	-0,05	-0,37
SS	-0,47	-0,47	0,18	0,36	0,39	0,74*	#	0,62*	0,25	-	0,44	0,45	0,52	0,41	-0,07	-0,29	0,5
TOC	0,02	-0,62*	0,41	0,67*	0,6*	0,65*	0,71*	#	-0,57*	-	0,79*	0,45	0,21	0,51	-0,29	-0,48	-0,06
FLOW	-0,55	0,61*	-0,79*	-0,28	-0,22	-0,15	0,2	-0,41	#	-	-0,22	0,01	0,11	-0,41	0,36	0,52*	0,32
S_{254}	-0,37	0,27	-0,08	-0,21	-0,24	0,23	0,61*	0,29	0,13	#	-0,07	0,05	-0,33	-0,19	0,81*	0,45	-0,52
FIX	-0,09	-0,09	0,23	0,28	0,33	0,1	0,45	0,52*	-0,31	0,32	#	0,83*	0,4	0,52*	-0,45	-0,29	0
BIX	-0,1	-0,12	0,21	0,22	0,28	0,09	0,52*	0,45	-0,16	0,37	0,91*	#	0,24	0,23	-0,27	0,02	-0,08
HIX	0,24	0,18	-0,08	0,19	0,21	-0,32	-0,3	0,07	-0,11	-0,38	0,29	0,2	#	0,35	-0,12	-0,34	0,71*
A_{254}	-0,35	-0,18	0,24	0,19	0,13	0,49*	0,75*	0,69*	-0,13	0,87*	0,43	0,39	-0,24	#	-0,57*	-0,73*	0
E2:E3	0,39	0,03	0,06	-0,03	-0,05	-0,57*	-0,67*	-0,48*	0,05	-0,67*	-0,3	-0,22	0,38	-0,76*	#	0,53*	0,2
Slope	0,02	0,31	-0,36	-0,28	-0,17	-0,42	-0,24	-0,56*	0,37	-0,34	-0,16	0,03	0,07	-0,55*	0,41	#	-0,16
C:T	0,25	-0,21	0,07	0,33	0,34	-0,08	0,02	-0,01	0,11	-0,5*	0,01	-0,14	0,64*	-0,32	0,35	0,06	#

6.3. Appendix 3: Spatial differences FDOM and CDOM.

The top right corner are *F45* samples correlations and bottom left corner are *UF* samples correlations in the table. Values with (*) are significantly different (p<0, 05).

FIX	1D	20E	21E	6E	7E	11M	2M	12N	4O	5O	16Z	14AC
1D	#	0*	0*	0*	0*	0,07	0,61	1	0*	0*	0*	0,79
20E	0,01*	#	0,68	0,77	1	0,02*	0*	0*	0,76	0,62	1	0*
21E	0*	0,62	#	0,01*	0,43	0*	0*	0*	0,01*	0*	0,11	0*
6E	0,88	0,25	0*	#	1	0,66	0*	0*	1	1	1	0*
7E	0,03*	1	0,77	0,41	#	0,34	0*	0*	1	0,99	1	0*
11M	1	0,07	0*	1	0,16	#	0*	0,04*	0,87	0,86	0,13	0*
2M	0*	0*	0*	0*	0*	0*	#	0,11	0*	0*	0*	1
12N	0,04*	0*	0*	0*	0*	0*	0,26	#	0*	0*	0*	0,43
4O	0,62	0,8	0,02*	1	0,87	0,98	0*	0*	#	1	1	0*
5O	1	0,04*	0*	1	0,11	1	0*	0*	0,96	#	0,98	0*
16Z	0,11	0,99	0,07	0,9	0,99	0,55	0*	0*	1	0,4	#	0*
14AC	0*	0*	0*	0*	0*	0*	1	0,68	0*	0*	0*	#

BIX	1D	20E	21E	6E	7E	11M	2M	12N	4O	5O	16Z	14AC
1D	#	0*	0*	0*	0*	0,27	0,96	1	0*	0*	0*	0,89
20E	0,17	#	0,95	0,97	1	0*	0*	0*	0,29	0,36	1	0*
21E	0*	0,9	#	0,2	0,96	0*	0*	0*	0,01*	0,01*	0,74	0*
6E	1	0,59	0,03*	#	0,99	0*	0*	0*	0,92	0,97	1	0*
7E	0,28	1	0,95	0,74	#	0*	0*	0*	0,53	0,63	1	0*
11M	1	0,03*	0*	0,93	0,1	#	0*	0,3	0,56	0,24	0*	0*
2M	0*	0*	0*	0*	0*	0*	#	0,5	0*	0*	0*	1
12N	0*	0*	0*	0*	0*	0*	0,81	#	0*	0*	0*	0,53
4O	1	0,51	0,03*	1	0,65	1	0*	0*	#	1	0,35	0*
5O	1	0,12	0*	1	0,25	1	0*	0*	1	#	0,43	0*
16Z	0,6	1	0,34	0,98	1	0,23	0*	0*	0,95	0,54	#	0*
14AC	0*	0*	0*	0*	0*	0*	1	0,91	0*	0*	0*	#

HIX	1D	20E	21E	6E	7E	11M	2M	12N	4O	5O	16Z	14AC
1D	#	1	0,22	1	1	0,97	0*	0*	1	1	0,9	0,91
20E	0*	#	0,24	1	1	0,98	0*	0*	1	1	0,92	0,89
21E	0,02*	1	#	0,03*	0,92	0,85	0*	0*	0,21	0,11	0,92	0*
6E	0*	0,22	0,78	#	0,9	0,56	0*	0*	1	1	0,32	0,97
7E	0,04*	1	1	0,18	#	1	0*	0*	1	0,99	1	0,37
11M	0,98	0,05	0,17	0*	0,39	#	0*	0*	0,98	0,9	1	0,13
2M	0*	0*	0*	0*	0*	0*	#	0,84	0*	0*	0*	0*
12N	0*	0*	0*	0*	0*	0*	1	#	0*	0*	0*	0,17
4O	0,53	0,65	0,76	0*	0,96	0,99	0*	0*	#	1	0,9	0,82
5O	0*	1	1	0,06	1	0,01*	0*	0*	0,49	#	0,72	0,85
16Z	0*	0,18	0,71	1	0,14	0*	0*	0,01*	0*	0,05*	#	0,07
14AC	0*	0,99	1	1	0,96	0*	0*	0*	0,13	0,98	0,99	#

C:T	1D	20E	21E	6E	7E	11M	2M	12N	4O	5O	16Z	14AC
1D	#	0*	0*	0*	0*	0*	0,98	0,95	0,02*	0,02*	0*	1
20E	0,95	#	1	1	1	0,73	0*	0*	0,44	0,25	1	0*
21E	1	1	#	1	0,92	0,2	0*	0*	0,08	0,04*	0,9	0*
6E	0,36	1	1	#	1	0,24	0*	0*	0,08	0,02*	1	0*
7E	0,32	0,99	0,99	1	#	1	0*	0*	0,97	0,92	1	0,03*
11M	1	1	1	0,83	0,72	#	0*	0*	1	1	0,92	0,1
2M	0*	0*	0*	0*	0*	0*	#	1	0*	0*	0*	0,88
12N	0*	0*	0*	0*	0*	0*	1	#	0*	0*	0*	0,8
4O	0,78	1	1	1	1	0,99	0*	0*	#	1	0,68	0,3
5O	0*	0,36	0,66	0,75	1	0,02*	0*	0*	0,59	#	0,43	0,3
16Z	0*	0,12	0,36	0,32	0,98	0*	0*	0*	0,23	1	#	0*
14AC	0*	0*	0,03*	0,02*	0,33	0*	0,39	0,16	0,01*	0,52	0,87	#

E2:E3	1D	20E	21E	6E	7E	11M	2M	12N	4O	5O	16Z	14AC
1D	#	0,16	0,01*	0*	0,02*	0,99	1	1	0,33	0,03*	0*	1
20E	0*	#	0,98	0,96	1	0,73	0,01*	0,22	1	1	0,94	0,06
21E	0*	0,29	#	1	1	0,11	0*	0,01*	0,83	0,99	1	0*
6E	0*	0,17	1	#	1	0,01*	0*	0*	0,6	0,97	1	0*
7E	0*	1	0,61	0,62	#	0,17	0*	0,02*	0,93	1	1	0,01*
11M	0,64	0*	0*	0*	0*	#	0,75	1	0,93	0,32	0,01*	0,87
2M	0*	0,62	0*	0*	0,57	0,24	#	0,99	0,03*	0*	0*	1
12N	0*	1	0,06	0,01*	1	0*	0,81	#	0,44	0,02*	0*	0,99
4O	0*	0,84	0*	0*	0,77	0,29	1	0,96	#	1	0,52	0,14
5O	0*	0,99	0,01*	0*	0,97	0,01*	0,99	1	1	#	0,93	0,01*
16Z	0*	0,06	1	1	0,37	0*	0*	0*	0*	0*	#	0*
14AC	0,02*	0,94	0,02*	0*	0,89	0,63	1	0,99	1	1	0*	#

Slope	1D	20E	21E	6E	7E	11M	2M	12N	4O	5O	16Z	14AC
1D	#	0,14	1	0*	0*	1	0,94	1	0,88	0,31	0*	0,24
20E	1	#	0,05*	0,36	0,94	0*	0,78	0,01*	0,96	1	0,12	0*
21E	0,85	0,29	#	0*	0*	1	0,63	1	0,53	0,12	0*	0,88
6E	0*	0,1	0*	#	1	0*	0*	0*	0*	0,01*	1	0*
7E	0,75	1	0,05	0,93	#	0*	0,04*	0*	0,16	0,47	1	0*
11M	0*	0*	0,74	0*	0*	#	0,2	1	0,17	0,01*	0*	0,63
2M	1	1	0,69	0*	0,71	0*	#	0,5	1	0,98	0*	0*
12N	0,65	0,06	1	0*	0*	0,07	0,27	#	0,44	0,02*	0*	0,26
4O	1	0,88	0,98	0*	0,33	0*	1	0,95	#	1	0*	0*
5O	1	0,99	0,77	0*	0,61	0*	1	0,39	1	#	0*	0*
16Z	0*	0,01*	0*	0,99	0,44	0*	0*	0*	0*	0*	#	0*
14AC	0,18	0,01*	1	0*	0*	1	0,06	0,98	0,43	0,09	0*	#

S_{254}	1D	20E	21E	6E	7E	11M	2M	12N	4O	5O	16Z	14AC
1D	#	1	1	0,83	0,91	0,55	0,15	0,15	0,99	1	1	0*
20E	0*	#	1	0,81	0,94	0,65	0,15	0,15	1	1	1	0*
21E	0*	1	#	0,89	0,99	0,89	0,31	0,31	1	1	1	0,01*
6E	0*	0,99	0,97	#	0,05*	0*	0,98	0,97	0,04*	1	0,55	0,1
7E	0*	0,98	1	0,38	#	1	0*	0*	1	0,36	0,9	0*
11M	0*	1	1	1	0,62	#	0*	0*	1	0,03*	0,44	0*
2M	0,01*	0,37	0,38	0,92	0,02*	0,93	#	1	0*	0,44	0,03*	0,51
12N	0*	0,88	0,84	1	0,16	1	1	#	0*	0,43	0,03*	0,52
4O	0*	1	0,99	1	0,56	1	0,95	1	#	0,47	0,99	0*
5O	0,01*	0,5	0,49	0,97	0,04*	0,97	1	1	0,98	#	0,99	0,02*
16Z	0*	1	1	0,62	1	0,91	0,02*	0,24	0,86	0,04*	#	0*
14AC	1	0*	0*	0,01*	0*	0,01*	0,21	0,04*	0,02*	0,17	0*	#

A_{254}	1D	20E	21E	6E	7E	11M	2M	12N	4O	5O	16Z	14AC
1D	#	0*	0*	0*	0*	0,45	1	0,98	0*	0*	0*	1
20E	0*	#	0,18	0,99	1	0,03*	0*	0*	0,96	1	0,89	0*
21E	0*	0,1	#	0,57	0,84	0*	0*	0*	0*	0,03*	0,9	0*
6E	0*	0,59	0,9	#	1	0*	0*	0*	0,16	0,8	1	0*
7E	0*	1	0,18	0,8	#	0*	0*	0*	0,53	0,96	1	0*
11M	0,4	0*	0*	0*	0*	#	0,07	0,98	0,6	0,02*	0*	0,07
2M	0,05	0*	0*	0*	0*	1	#	0,72	0*	0*	0*	1
12N	0*	0,09	0*	0*	0,22	0,22	0,73	#	0,03*	0*	0*	0,51
4O	0*	0,16	0*	0*	0,31	0,39	0,86	1	#	0,99	0,03*	0*
5O	0*	0,98	0*	0*	0,99	0*	0*	0,62	0,76	#	0,37	0*
16Z	0*	0,22	1	1	0,44	0*	0*	0*	0*	0*	#	0*
14AC	0,47	0,01*	0*	0*	0,02*	1	1	0,9	0,94	0,07	0*	#